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LXXIV. *A Method for the Solution of Oscillation Problems by Matrices.* By W. J. DUNCAN, D.Sc., A.M.I.Mech.E., and A. R. COLLAR, B.A., B.Sc., of the Aerodynamics Department, The National Physical Laboratory *.

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* Communicated by E. F. Relf, A.R.C.Sc.

§1. *Introduction and Summary* *.

THE present paper gives an account of an arithmetical process for the solution of a large class of problems concerning the oscillations of dynamical systems. While the proof of the correctness of the method depends on the theory of matrices, and the matrix notation is very concise and convenient for the formulation of the method, yet the process of solution is a simple one which can be used even by those who are quite ignorant of the theory of matrices.

The method as hitherto developed is subject to the limitation that it can only be applied to dynamical systems where dissipative or "motional" forces are absent. On the other hand, it is considered that the following advantages may fairly be claimed for the method :—

- (1) The arithmetical labour involved in the solution is greatly reduced, more especially when only the fundamental mode of oscillation is required.
- (2) As a corollary to the last, it becomes practicable to deal with systems having a very large number of degrees of freedom. An application to a system having twenty degrees of freedom is given in §11, and systems of much greater complexity could be treated without difficulty.
- (3) The method is entirely free from tentative processes.
- (4) The correctness of the final solution is checked automatically in the course of the solution †.
- (5) An error, however large, occurring at any stage does not affect the accuracy of the final solution †. The only adverse effect of an error is to prolong the calculation.

On account of (2), the method lends itself particularly well to the approximate treatment of continuous systems. Examples are given in §§ 9, 10, and 11. In all three examples the exact solution for the continuous system is known, and the approximate solution obtained by the matrix method using ten or twenty degrees of freedom proves to be very closely correct.

* The Authors are indebted to the Aeronautical Research Committee for permission to communicate the paper.

† This is subject to the proviso that no errors have been made in the preliminary calculation of the elements of the dynamical matrix.

In the general formulation of the method the dynamical equations are obtained in a novel form, but they are, of course, equivalent to the Lagrangian equations, and can be derived from the latter by a definite transformation. The physical notion used in deriving the new dynamical equations is that any generalized displacement is equal to the sum of the products of the generalized forces and the appropriate "flexibility coefficients," where it is to be understood that the generalized forces include the inertia forces. In many cases the coefficients in the dynamical equations of this kind can be obtained directly with less labour than those in the ordinary Lagrangian equations.

§ 2. Elementary Sketch of the Method.

A formal exposition of the method is given in §§ 3, 4, and 5, but this will be approached by an application to a particular problem of elementary dynamics. It is hoped that the principles of the method, which are of a very simple nature, will in this way be made clear to the reader before he reaches the more mathematical parts of the paper.

Consider the small oscillations of a triple pendulum (see fig. 1). For simplicity it will be assumed that the three bob-weights are massive particles and that the connecting-shanks are massless. Also the articulations will be supposed to coincide with the positions of the particles 1 and 2.

Let a horizontal force of unit magnitude be applied to the particle 1. When the system is in equilibrium under the action of this force let the horizontal displacements of the particles be f_{11} , f_{21} , f_{31} . Similarly, let the displacements under unit loads applied at the particles 2 and 3 be f_{12} , f_{22} , f_{32} , and f_{13} , f_{23} , f_{33} respectively. The actual values of these "flexibility coefficients" will be obtained later, but are not required at the present stage of the argument. The set of nine coefficients may be made the elements of a square matrix $[f]$ which will be called the "flexibility matrix":—

$$[f] \equiv \begin{bmatrix} f_{11} & f_{12} & f_{13} \\ f_{21} & f_{22} & f_{23} \\ f_{31} & f_{32} & f_{33} \end{bmatrix} \dots \dots \dots \quad (1)$$

Now suppose that forces P_1, P_2, P_3 act upon the particles 1, 2, 3 respectively. Then the displacements when the system is in equilibrium will be

$$\left. \begin{aligned} x_1 &= f_{11}P_1 + f_{12}P_2 + f_{13}P_3 \\ x_2 &= f_{21}P_1 + f_{22}P_2 + f_{23}P_3 \\ x_3 &= f_{31}P_1 + f_{32}P_2 + f_{33}P_3 \end{aligned} \right\} \quad \dots \quad (2)$$

Fig. 1.

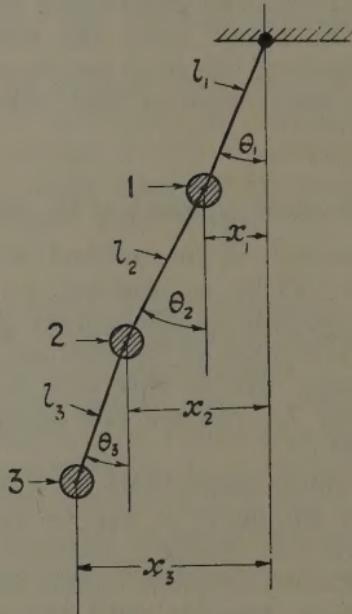


Diagram of triple pendulum.

Single column matrices can be constructed from the forces P and the displacements x . Thus the force or load matrix is

$$[P] = \begin{bmatrix} P_1 \\ P_2 \\ P_3 \end{bmatrix}, \quad \dots \quad (3)$$

and the displacement matrix is

$$[x] = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}, \quad \dots \quad (4)$$

Now form the matrix product $[f][P]$. By the multiplication rule this is a single column matrix whose elements are the expressions which appear on the right of equations (2).

Hence these three linear equations are equivalent to the single matrix equation

$$[x] = [f][P], \quad \dots \dots \dots \quad (5)$$

where the product on the right cannot be commuted.

The matrix equation (5) can be applied to the free oscillations of the system if the "inertia forces," *i.e.*, the reversed mass accelerations, are substituted for the applied forces P . Thus, if m_1, m_2, m_3 be the masses of the particles, the three dynamical equations can be replaced by the single matrix equation

$$[x] = [f][-m\ddot{x}], \quad \dots \dots \dots \quad (6)$$

where

$$[-m\ddot{x}] = \begin{pmatrix} -m_1\ddot{x}_1 \\ -m_2\ddot{x}_2 \\ -m_3\ddot{x}_3 \end{pmatrix}. \quad \dots \dots \dots \quad (7)$$

Equation (6) can be written in another form which is sometimes more convenient. For if $[m]$ be the diagonal matrix

$$\begin{pmatrix} m_1 & 0 & 0 \\ 0 & m_2 & 0 \\ 0 & 0 & m_3 \end{pmatrix}, \quad \dots \dots \dots \quad (8)$$

then

$$[m\ddot{x}] = [m][\ddot{x}]. \quad \dots \dots \dots \quad (9)$$

Equation (6) now becomes

$$[x] = -[f][m][\ddot{x}], \quad \dots \dots \dots \quad (10)$$

$$= -[D][\ddot{x}], \quad \dots \dots \dots \quad (11)$$

where $[D]$ is what may be called the dynamical matrix. The full expression for this matrix is

$$\begin{aligned} [D] &= [f][m], \\ &= \begin{pmatrix} f_{11}m_1 & f_{12}m_2 & f_{13}m_3 \\ f_{21}m_1 & f_{22}m_2 & f_{23}m_3 \\ f_{31}m_1 & f_{32}m_2 & f_{33}m_3 \end{pmatrix}. \quad \dots \dots \quad (12) \end{aligned}$$

Now suppose that the system is oscillating in a single mode, so that all the particles describe simple harmonic motions with the common frequency f . If $p = 2\pi f$, then $\ddot{x}_1 = -p^2 x_1$, etc., and equation (11) now becomes

$$[x] = p^2[D][x], \quad \dots \dots \dots \quad (13)$$

This matrix equation is equivalent to the three ordinary equations

$$\left. \begin{aligned} x_1 \left(f_{11}m_1 - \frac{1}{p^2} \right) + x_2 f_{12}m_2 + x_3 f_{13}m_3 &= 0 \\ x_1 f_{21}m_1 + x_2 \left(f_{22}m_2 - \frac{1}{p^2} \right) + x_3 f_{23}m_3 &= 0 \\ x_1 f_{31}m_1 + x_2 f_{32}m_2 + x_3 \left(f_{33}m_3 - \frac{1}{p^2} \right) &= 0 \end{aligned} \right\}. \quad (14)$$

Put

$$\lambda = \frac{1}{p^2}. \quad \dots \quad (15)$$

Then the foregoing homogeneous linear equations in the displacements will be compatible if λ is a root of the determinantal equation

$$\begin{vmatrix} \lambda - f_{11}m_1 & -f_{12}m_2 & -f_{13}m_3 \\ -f_{21}m_1 & \lambda - f_{22}m_2 & -f_{23}m_3 \\ -f_{31}m_1 & -f_{32}m_2 & \lambda - f_{33}m_3 \end{vmatrix} = 0. \quad (16)$$

The array of constants in (16) is the same as in [D] except for a change of sign, and λ appears only in the principal diagonal. The equation (16) is spoken of as the "characteristic equation" of the matrix [D]. Thus the frequencies in the several modes are determined by the roots of the characteristic equation (these are known as the "latent roots"), and the amplitude ratios are determinable from equations (14).

The orthodox method for the solution of the matrix equation (13) consists in finding the latent roots and then solving the linear equations (14). However, the fundamental frequency and the amplitude ratios in that mode* can be obtained very easily by a process of successive substitution in the matrix equation. Take an arbitrary initial set of amplitudes † represented by the matrix $[x]_0$, and form the product

$$[D][x]_0 = [x]_1, \quad \text{say.} \quad \dots \quad (17)$$

Next, substitute $[x]_1$ for $[x]_0$ and so find

$$[x]_2 = [D][x]_1 = [D]^2[x]_0. \quad \dots \quad (18)$$

* With regard to the overtones, see §7.

† The set must not be actually incompatible with the presence of the fundamental, but this restriction is of no practical importance (see §5).

The process of successive substitution can be carried on indefinitely, and it can be shown (see § 5) that the ratios of the elements in $[x]$, tend to assume constant values appropriate to the fundamental mode, while the ratio of a pair of *corresponding* elements in $[x]_r$ and $[x]_{r-1}$ tends to the value of $\lambda = \frac{1}{p^2}$ for the fundamental. As a rule the convergence is very rapid, so that the number of substitutions required to give an accuracy of, say, 1 in 1000, is quite small.

In order to illustrate the process of solution a numerical example will be given, and as a first step it will be necessary to obtain the values of the flexibility coefficients. These are very easily deduced by the aid of the following principles :—

(a) The tension at any point of the pendulum is equal to the total weight of the particles below the point.

(b) The horizontal component of the tension at any point is equal to the total lateral force applied below the point.

(c) It follows from (b) that if a single force is applied at a certain particle, then all the particles below it have the same displacement as that particle.

(d) It also readily follows from (b) that the displacement of a given particle is the same for all points of application of a given force *below* the particle.

By (c)

$$f_{31} = f_{21} = f_{11}$$

and $f_{32} = f_{22}$.

Also by (d)

$$f_{11} = f_{12} = f_{13}$$

and $f_{22} = f_{23}$.

By combination of these equations

$$f_{31} = f_{13} = f_{21} = f_{12} = f_{11}, \dots \quad (19)$$

and $f_{32} = f_{23} = f_{22}, \dots \quad (20)$

Thus the flexibility coefficients have only three distinct values. These may be taken as f_{13}, f_{23}, f_{33} , and they may

be found by considering the case where unit horizontal force is applied to particle 3. By (a) and (b)

$$gm_3\theta_3 = g(m_2+m_3)\theta_2 = g(m_1+m_2+m_3)\theta_1 = 1. \quad (21)$$

These equations determine the angles θ and therefore also the displacements (flexibility coefficients), since (see fig. 1)

$$f_{13} = x_1 = l_1\theta_1 = \frac{l_1}{g(m_1+m_2+m_3)}, \quad \dots \quad (22)$$

$$f_{23} = x_2 = x_1 + l_2\theta_2 = \frac{l_1}{g(m_1+m_2+m_3)} + \frac{l_2}{g(m_2+m_3)}, \quad \dots \quad (23)$$

and

$$f_{33} = x_3 = x_2 + l_3\theta_3 = \frac{l_1}{g(m_1+m_2+m_3)} + \frac{l_2}{g(m_2+m_3)} + \frac{l_3}{gm_3}. \quad \dots \quad (24)$$

Suppose now that

$$m_1 = m_2 = m_3 = m,$$

and that

$$l_1 = l_2 = l_3 = l.$$

Then by equations (19) to (24) the values of the flexibility coefficients are as follows:—

$$f_{31} = f_{13} = f_{21} = f_{12} = f_{11} = \frac{l}{3gm},$$

$$f_{32} = f_{23} = f_{22} = \frac{5l}{6gm},$$

$$\text{and } f_{33} = \frac{11l}{6gm}.$$

Accordingly the dynamical matrix is by equation (12)

$$[D] = \frac{l}{6g} \begin{bmatrix} 2 & 2 & 2 \\ 2 & 5 & 5 \\ 2 & 5 & 11 \end{bmatrix}, \quad \dots \quad (25)$$

and the matrix equation (13) becomes

$$\varpi \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} 2 & 2 & 2 \\ 2 & 5 & 5 \\ 2 & 5 & 11 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}, \quad \dots \quad (26)$$

where

$$\varpi = \frac{6g}{p^2 l}. \quad \dots \quad (27)$$

Now select an arbitrary set of elements for $[x]_0$, say

$$x_1 = x_2 = x_3 = 1.$$

Then

$$\begin{pmatrix} 2 & 2 & 2 \\ 2 & 5 & 5 \\ 2 & 5 & 11 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 6 \\ 12 \\ 18 \end{pmatrix} = 18 \begin{pmatrix} 1/3 \\ 2/3 \\ 1 \end{pmatrix},$$

Successive substitution yields

$$\begin{pmatrix} 2 & 2 & 2 \\ 2 & 5 & 5 \\ 2 & 5 & 11 \end{pmatrix} \begin{pmatrix} 1/3 \\ 2/3 \\ 1 \end{pmatrix} = \begin{pmatrix} 4 \\ 9 \\ 15 \end{pmatrix} = 15 \begin{pmatrix} 4/15 \\ 9/15 \\ 1 \end{pmatrix},$$

$$\begin{pmatrix} 2 & 2 & 2 \\ 2 & 5 & 5 \\ 2 & 5 & 11 \end{pmatrix} \begin{pmatrix} 4/15 \\ 9/15 \\ 1 \end{pmatrix} = \begin{pmatrix} 3\frac{1}{5} \\ 8\frac{8}{15} \\ 14\frac{8}{15} \end{pmatrix} = 14.53 \begin{pmatrix} 0.256881 \\ 0.587156 \\ 1.0 \end{pmatrix},$$

and

$$\begin{pmatrix} 2 & 2 & 2 \\ 2 & 5 & 5 \\ 2 & 5 & 11 \end{pmatrix} \begin{pmatrix} 0.256881 \\ 0.587156 \\ 1.0 \end{pmatrix} = 14.4495 \begin{pmatrix} 0.255238 \\ 0.584762 \\ 1.0 \end{pmatrix}.$$

TABLE I.

Determination of Fundamental Mode and Frequency of a Triple Pendulum by Successive Multiplication by the Dynamical Matrix.

Approximation.	5th.	6th.	7th.	8th.	9th.	10th.
x_1	0.254949	0.254897	0.254887	0.254885	0.254885	0.254885
x_2	0.584323	0.584243	0.584229	0.584226	0.584225	0.584225
x_3	1.0	1.0	1.0	1.0	1.0	1.0
ω	14.4343	14.4315	14.4310	14.4309	14.4309	14.4309

The result of four substitutions is already very closely correct, although the assumed initial mode obviously differs greatly from the fundamental. The process can be carried on till the numbers repeat to, say, six figures. As shown in Table I., the 10th approximation is identical with the 9th, so that the solution verifies itself. Its correctness has further been checked by solution of the

Lagrangian equations of motion of the system in the ordinary way.

It has already been pointed out that the process of successive substitution is equivalent to multiplying the arbitrarily assumed initial matrix $[x]_0$ by a power of the dynamical matrix $[D]$. Since the product converges to a definite form, it is evident that $[D]^r$ must do the same. Repeated squaring gives *

$$[D]^8 = 1296 \begin{pmatrix} 67044 & 153672 & 263034 \\ 153672 & 352233 & 602904 \\ 263034 & 602904 & 1031973 \end{pmatrix}, \quad (28)$$

and one further multiplication by $[D]$ yields

$$[D]^9 = 1296 \begin{pmatrix} 967500 & 2217618 & 3795822 \\ 2217618 & 5083029 & 8700453 \\ 3795822 & 8700453 & 14892291 \end{pmatrix}. \quad (29)$$

TABLE II.

Ratios of the Elements of $[D]^9$ to the Corresponding Elements of $[D]^8$.

14.4308	14.4309	14.4309
14.4309	14.4309	14.4309
14.4309	14.4309	14.4309

The numbers which appear in these matrices are remarkable in several respects. Firstly, the ratios of corresponding elements are the same to a high degree of accuracy (see Table II.).

Secondly, the elements in the first and second rows of the matrices are almost exactly proportional to the corresponding elements of the bottom row. Thus for $[D]^9$ the ratios of the elements in the first row to those in the third are

$$\frac{967500}{3795822} = 0.254885. \quad \frac{2217618}{8700453} = 0.254885.$$

$$\frac{3795822}{14892291} = 0.254885.$$

* The powers of $(l/6g)$ are omitted for convenience.

Also the ratios of the elements in the second and third rows are

$$\frac{2217618}{3795822} = 0.584226. \quad \frac{5083029}{8700453} = 0.584226.$$

$$\frac{8700453}{14892291} = 0.584225.$$

It is now evident * that any high power $[D]^r$ of the dynamical matrix can be written in the form

$$\varpi^r \begin{bmatrix} \alpha A & \alpha B & \alpha C \\ \beta A & \beta B & \beta C \\ A & B & C \end{bmatrix}, \quad \dots \quad (30)$$

where ϖ , A, B, C, α , and β are constants. Now the product of this matrix and an arbitrary initial amplitude matrix $[x]_0$ is

$$\varpi^r \begin{bmatrix} \alpha A & \alpha B & \alpha C \\ \beta A & \beta B & \beta C \\ A & B & C \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \varpi^r \begin{bmatrix} \alpha(Ax_1 + Bx_2 + Cx_3) \\ \beta(Ax_1 + Bx_2 + Cx_3) \\ (Ax_1 + Bx_2 + Cx_3) \end{bmatrix}, \quad \dots \quad (31)$$

and the elements of the product are in the ratio $\alpha : \beta : 1$ whatever may be the values of x_1 , x_2 , and x_3 (provided that $Ax_1 + Bx_2 + Cx_3 \neq 0$). The convergence of the amplitude ratios to constants which are independent of the mode initially assumed is now explained. Further, the constant ϖ obviously determines the frequency of the oscillation (see equation (27)).

The foregoing discussion shows that the problem can be solved merely by raising the dynamical matrix to some fairly high power, without operating on an arbitrary amplitude matrix. However, the arithmetical labour is greatly reduced in the method of successive substitution, since only columnar instead of square matrices have to be calculated.

§ 3. Generalised Flexibility Coefficients and the Equations of Motion.

The system discussed in § 2 is of a particularly simple nature, since it may be considered to be constructed

* The proof is given in § 5.

from physical units (in this case particles) each of which has only a single degree of freedom. Systems of this type are of great technical importance; some examples are loaded beams, loaded membranes or plates, shafts with fly-wheels, etc. All such cases can be treated in exactly the same manner as the triple pendulum, but the method of solution by matrices is capable of a much wider application. The exposition which follows is concerned with the undamped oscillations of a conservative system having a finite number of degrees of freedom, whose dynamical coefficients can be treated as constants for the range of displacements considered, but which is otherwise of unrestricted type.

The special simplicity of the triple pendulum arises from the fact that the flexibility coefficients have unique values. In general, however, the values of these coefficients will depend on the point of application of the unit force. But it is always possible to find a set of generalized flexibility coefficients with constant values, as will now be explained.

Take the equilibrium configuration of the system as the datum or zero for the measurement of the generalized coordinates $\phi_1, \phi_2, \dots, \phi_n$. Then if the system is displaced by the action of external forces, the potential energy of the system will be increased by a quantity which is a homogeneous quadratic function of the coordinates, say,

$$V = \frac{1}{2}c_{11}\phi_1^2 + \frac{1}{2}c_{22}\phi_2^2 + \dots + c_{12}\phi_1\phi_2 + c_{13}\phi_1\phi_3 + \dots + c_{23}\phi_2\phi_3 + \text{etc.} \quad (32)$$

Now the generalized force P_r , corresponding to the coordinate ϕ_r , is defined as the rate of increase of V with ϕ_r when this coordinate alone receives a small increment, *i. e.*,

$$P_r = \frac{\partial V}{\partial \phi_r}. \quad \dots \quad \dots \quad \dots \quad \dots \quad (33)$$

The set of n linear equations (33) can be solved for the displacements, and the resulting equations may be written

$$\phi_s = f_{s1}P_1 + f_{s2}P_2 + \text{etc.}, \quad \dots \quad \dots \quad \dots \quad (34)$$

where the constants f will be called the generalized flexibility coefficients. Let

$$\Delta = \begin{vmatrix} c_{11} & c_{12} & \dots & c_{1n} \\ c_{21} & c_{22} & \dots & c_{2n} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ c_{n1} & c_{n2} & \dots & c_{nn} \end{vmatrix}, \quad \dots \quad (35)$$

where $c_{pq} = c_{qp}$, and let Δ_{st} be the cofactor of c_{st} in Δ . Then

$$f_{st} = \frac{\Delta_{ts}}{\Delta}. \quad \dots \quad (36)$$

On account of the symmetry of Δ it follows that

$$f_{st} = f_{ts}. \quad \dots \quad (37)$$

Now by Euler's theorem, equations (33) yield

$$\begin{aligned} V &= \frac{1}{2} \sum \phi_r P_r \\ &= \frac{1}{2} f_{11} P_1^2 + \frac{1}{2} f_{22} P_2^2 + \text{etc.} \\ &\quad + f_{12} P_1 P_2 + f_{13} P_1 P_3 + \dots + f_{23} P_2 P_3 + \text{etc.} \end{aligned} \quad (38)$$

on account of equations (34) and (37). Thus if the expression for V is known as a function either of the generalized displacements or of the generalized forces, then the values of the generalized flexibility coefficients can be found.

It is now necessary to find the expressions for the generalized forces in terms of the external forces applied to the system. By the definition of P_r , the product $P_r d\phi_r$ is equal to the work done on the system by the external forces in a virtual displacement corresponding to the increment $d\phi_r$ in ϕ_r . Let (x, y, z) be the cartesian coordinates of the point of application of the external force (X, Y, Z) . Then the whole work done in the virtual displacement is

$$\Sigma (X \delta x + Y \delta y + Z \delta z).$$

Hence

$$P_r = \Sigma \left(X \frac{\partial x}{\partial \phi_r} + Y \frac{\partial y}{\partial \phi_r} + Z \frac{\partial z}{\partial \phi_r} \right). \quad \dots \quad (39)$$

When the system is in motion the displacement equations (34) will remain valid provided that the inertia

forces (reversed mass-accelerations) of the particles composing the system are included among the applied forces. Hence the expression for P_r becomes

$$P_r = \Sigma \left(X \frac{\partial x}{\partial \phi_r} + Y \frac{\partial y}{\partial \phi_r} + Z \frac{\partial z}{\partial \phi_r} \right) - \Sigma \left(\ddot{x} \frac{\partial x}{\partial \phi_r} + \ddot{y} \frac{\partial y}{\partial \phi_r} + \ddot{z} \frac{\partial z}{\partial \phi_r} \right) \delta m, \dots \quad (40)$$

where δm is an element of mass. But

$$\ddot{x} = \Sigma_q \frac{\partial x}{\partial \phi_q} \ddot{\phi}_q, \dots \quad (41)$$

since $\partial x / \partial \phi_q$ is independent of time. Hence

$$P_r = \Sigma \left(X \frac{\partial x}{\partial \phi_r} + Y \frac{\partial y}{\partial \phi_r} + Z \frac{\partial z}{\partial \phi_r} \right) - \Sigma_q \ddot{\phi}_q \Sigma \left(\frac{\partial x}{\partial \phi_r} \frac{\partial x}{\partial \phi_q} + \frac{\partial y}{\partial \phi_r} \frac{\partial y}{\partial \phi_q} + \frac{\partial z}{\partial \phi_r} \frac{\partial z}{\partial \phi_q} \right) \delta m. \dots \quad (42)$$

The coefficients of the generalized accelerations in the last equation are the inertial constants in the Lagrangian equations of motion, as is obvious from the manner in which the coefficients have been derived. Suppose that the kinetic energy of the system is given by

$$T = \frac{1}{2} a_{11} \dot{\phi}_1^2 + \frac{1}{2} a_{22} \dot{\phi}_2^2 + \dots + a_{12} \phi_1 \dot{\phi}_2 + a_{13} \phi_1 \dot{\phi}_3 + \dots + a_{23} \dot{\phi}_2 \dot{\phi}_3 + \dots \quad (43)$$

Then equation (42) can be written

$$P_r = P'_r - \Sigma_q a_{rq} \ddot{\phi}_q, \dots \quad (44)$$

where P'_r is the contribution of the external forces to P_r . Hence by equation (34) the typical dynamical equation is

$$\begin{aligned} \phi_s &= - \sum_t f_{st} \sum_q a_{tq} \ddot{\phi}_q + \sum_t f_{st} P'_t, \\ &= - \sum_q D_{sq} \ddot{\phi}_q + \sum_t f_{st} P'_t, \dots \quad (45) \end{aligned}$$

where

$$D_{sq} = \sum_t f_{st} a_{tq}, \dots \quad (46)$$

§ 4. The Equations of Motion in Matrix Notation.

The set of n equations (45) is equivalent to the single matrix equation

$$[\ddot{\phi}] = -[\mathbf{D}][\ddot{\phi}] + [f][\mathbf{P}'], \dots \quad (47)$$

where

$$[\mathbf{D}] = \begin{bmatrix} D_{11} & D_{12} & \dots & D_{1n} \\ D_{21} & D_{22} & \dots & D_{2n} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ D & D_{n2} & \dots & D_{nn} \end{bmatrix}. \dots \quad (48)$$

Also (46) shows that

$$[\mathbf{D}] = [f][a], \dots \quad (49)$$

while in accordance with the definition of the inverse of a matrix

$$[f] = [c]^{-1} \dots \quad (50)$$

by equations (35) and (36). Hence

$$[\mathbf{D}] = [c]^{-1}[a], \dots \quad (51)$$

and the dynamical equation (47) becomes

$$[\ddot{\phi}] = -[c]^{-1}[a][\ddot{\phi}] + [c]^{-1}[\mathbf{P}']. \dots \quad (52)$$

The last equation can be deduced directly from the Lagrangian equations of motion. For, if the terms in the accelerations are taken over to the right-hand side, the typical equation of motion can be written

$$\sum_q c_{r_q} \phi_q = -\sum_q a_{r_q} \ddot{\phi}_q + \mathbf{P}'_r. \dots \quad (53)$$

The set of equations (53) can be replaced by the matrix equation

$$[c][\ddot{\phi}] = -[a][\ddot{\phi}] + [\mathbf{P}'], \dots \quad (54)$$

and on multiplication throughout by $[c]^{-1}$ equation (52) is immediately obtained *. While the dynamical equation (52) can thus be deduced by a much more expeditious method than that already given, yet the more extended argument is thought to be of value as a help towards the better understanding of the physical meaning of the final dynamical equation. It may be added that it is

* It is clear from this that $[f]$ need not be symmetrical, *i.e.*, the equations hold even for non-conservative systems.

often more convenient to obtain $[D]$ directly than by transformation of the Lagrangian equations.

§ 5. *Solution of the Problem of Free Oscillation
by the Method of Successive Substitution.*

When external forces are absent, equation (47) becomes

$$[\phi] = -[D][\ddot{\phi}], \quad \dots \dots \quad (55)$$

and if the system is oscillating purely in one mode with frequency $p/2\pi$, this reduces to

$$[\phi] = p^2[D][\phi], \quad \dots \dots \quad (56)$$

which is of exactly the same form as equation (13). The theory of the solution of (56) by the method of successive substitution will now be given.

As already remarked in § 2, the result of a train of successive substitutions, beginning with an arbitrary matrix $[\phi]_0$, is equivalent to the determination of $[D]^{(n)}[\phi]_0$. Now by a general theorem on matrices (see Theorem I. of Appendix I.) any rational function of a square matrix $[u]$ of the n th order can be expressed as follows :—

$$f([u]) = \sum_{r=1}^n f(\lambda_r)[Z_r], \quad \dots \dots \quad (57)$$

where

$$[Z_r] = \frac{\prod(\lambda_s I - [u])}{\prod(\lambda_s - \lambda_r)}, \quad \dots \dots \quad (58)$$

and the n quantities λ are the “latent roots” of $[u]$. The continued products which appear in the numerator and denominator of (58) are to be taken for all values of λ_s with the exception of λ_r . Before the argument can be carried further it will be necessary to examine the nature of the latent roots in the present instance.

If

$$\lambda = \frac{1}{p^2}, \quad \dots \dots \quad (59)$$

then the matrix equation (56) is equivalent to the set of n homogeneous linear equations

$$\begin{aligned} (\lambda - D_{11})\phi_1 - D_{12}\phi_2 - D_{13}\phi_3 - \text{etc.} &= 0, \\ -D_{21}\phi_1 + (\lambda - D_{22})\phi_2 - D_{23}\phi_3 - \text{etc.} &= 0, \end{aligned} \quad \dots \quad (60)$$

and so on. In order that these may be compatible it is

necessary that λ should be a root of the determinantal equation

$$\begin{vmatrix} (\lambda - D_{11}) & -D_{12} & -D_{13} & \dots & -D_{1n} \\ -D_{21} & (\lambda - D_{22}) & -D_{23} & \dots & -D_{2n} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ -D_{n1} & -D_{n2} & \dots & \dots & (\lambda - D_{nn}) \end{vmatrix} = 0. \quad (61)$$

This is, by definition, the characteristic equation of the matrix $[D]$, and the roots are the latent roots. Since, by (59), the latent roots determine the frequencies in the n separate modes of the system, it is evident that in the present instance they must all be real positive numbers *. Let the roots be $\lambda_1, \lambda_2, \dots, \lambda_n$ in descending order of magnitude. (It will be assumed at present that all the roots are unequal.) Then only real numbers appear in the formula (57), and when $f([u]) = [u]^m$, this becomes

$$[u]^m = \sum_{r=1}^{r=n} \lambda_r^m [Z_r]. \quad \dots \quad (62)$$

But when m is large, all the terms on the right-hand side of this equation will be negligible compared to the first. Thus the limiting form of $[D]^m$ when m becomes large is

$$[D]^m = \frac{\lambda_1^m [D_1]}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \dots (\lambda_n - \lambda_1)}, \quad \dots \quad (63)$$

where

$$[D_1] = (\lambda_2 I - [D])(\lambda_3 I - [D]) \dots (\lambda_n I - [D]), \quad \dots \quad (64)$$

and λ_1 is the latent root corresponding to the fundamental mode. But, by the Cayley-Hamilton theorem,

$$[D_1](\lambda_1 I - [D]) = 0. \quad \dots \quad (65)$$

Now the cofactors of the elements in the determinant of the matrix $(\lambda_1 I - [D])$ are not all zero. Hence by Theorem II. of Appendix 1, it follows that $[D_1]$ is of the type

$$\begin{bmatrix} \alpha_1 A_1 & \alpha_1 A_2 & \dots & \alpha_1 A_n \\ \alpha_2 A_1 & \alpha_2 A_2 & \dots & \alpha_2 A_n \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \alpha_n A_1 & \alpha_n A_2 & \dots & \alpha_n A_n \end{bmatrix} \quad \dots \quad (66)$$

* The latent roots are, of course, the reciprocals of the roots of the ordinary Lagrange determinant. A formal proof of the reality of the roots is given in Routh's 'Rigid Dynamics,' 6th ed. vol. ii. p. 49.

In order to find the ratios α , commute the product in (65), as is permissible, since $[D_1]$ and $(\lambda_1 I - [D])$ are functions of the matrices $[D]$ and I only. Then the conditions that the elements in the first column of the commuted product shall vanish are, on cancellation of the common factor A_1 :—

$$\begin{aligned} (\lambda_1 - D_{11})\alpha_1 - D_{12}\alpha_2 - \text{etc.} &= 0, \\ - D_{21}\alpha_1 + (\lambda_1 - D_{22})\alpha_2 - \text{etc.} &= 0, \\ &\text{etc.} \end{aligned} \quad \quad \quad (67)$$

By comparison with equations (60) it is evident that the quantities α are proportional to the amplitudes in the several degrees of freedom in the fundamental mode. Finally, when m is large,

$$\begin{aligned} [D]^m [\phi]_0 &= \frac{\lambda_1^m}{\prod_{r \neq 1} (\lambda_r - \lambda_1)} \begin{bmatrix} \alpha_1 A_1 & \alpha_1 A_2 & \dots \\ \alpha_2 A_1 & \alpha_2 A_2 & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \\ \alpha_n A_1 & \alpha_n A_2 & \dots \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \dots \\ \dots \\ \phi_n \end{bmatrix} \\ &= \frac{\lambda_1^m}{\prod_{r \neq 1} (\lambda_r - \lambda_1)} \begin{bmatrix} \alpha_1 R_1 \\ \alpha_2 R_1 \\ \dots \\ \dots \\ \alpha_n R_1 \end{bmatrix}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (68) \end{aligned}$$

where

$$R_1 = A_1 \phi_1 + A_2 \phi_2 + \dots + A_n \phi_n.$$

Hence, subject to the provisos that the frequencies in the several modes are all different, and that the arbitrarily assumed initial mode does not make R_1 zero, the result of any large number of repeated substitutions gives the amplitude ratios in the fundamental mode, and the ratio of corresponding elements in a pair of consecutive amplitude matrices gives λ_1 , and therefore the fundamental frequency.

It will appear in §7 that the values of the coefficients A are required for the determination of the overtones. These coefficients can evidently be obtained by raising the dynamical matrix to a high power, but they are most conveniently found by a process of successive substitution which involves comparatively little labour. Let

$$[\psi] = [\psi_1 \psi_2 \dots \psi_n]$$

be an arbitrary line matrix. Then, when m is large,

$$[\psi][D]^m = \frac{\lambda_1^m [\psi][D_1]}{\prod_{r \neq 1} (\lambda_r - \lambda_1)}.$$

But by equation (66)

$$[\psi][D_1] = S_1[A_1 A_2 \dots A_n],$$

where $S_1 = \sum \psi_r \alpha_r$. Hence, whatever initial $[\psi]$ is chosen, the result of continued postmultiplication by $[D]$ is a line matrix whose elements are proportional to the coefficients A_r . This process is equivalent to continued premultiplication of the *columnar* matrix of the ψ 's by the *transposed* dynamical matrix.

§ 6. Remarks on the Cases where a Latent Root is repeated.

In § 5 it was assumed that the latent roots of the dynamical matrix were all distinct. Suppose, however, that $\lambda_{i+1} = \lambda_q$. Then two of the terms in (57) become infinite and the formula fails, but a suitable modification can be obtained by the substitution $\lambda_{i+1} = \lambda_i + \epsilon$, and determination of the limit as $\epsilon \rightarrow 0$ in the usual way.

For conciseness write

$$P(\lambda_q) = \frac{1}{(\lambda_1 - \lambda_q)(\lambda_2 - \lambda_q) \dots (\lambda_{q-1} - \lambda_q)(\lambda_{q+2} - \lambda_q) \dots (\lambda_n - \lambda_q)}, \quad \dots \quad (69)$$

and

$$[Q_q] = (\lambda_1 I - [u]) \dots (\lambda_{q-1} I - [u]) (\lambda_{q+2} I - [u]) \dots (\lambda_n I - [u]). \quad \dots \quad (70)$$

Then (see equation (58))

$$[Z_q] = \frac{P(\lambda_q)[Q_q](\lambda_q + \epsilon I - [u])}{\epsilon}, \quad \dots \quad (71)$$

and

$$[Z_{q+1}] = - \frac{P(\lambda_q + \epsilon)[Q_q](\lambda_q I - [u])}{\epsilon}. \quad \dots \quad (72)$$

Hence

$$\begin{aligned}
 & f(\lambda_q)[Z_q] + f(\lambda_{q+1})[Z_{q+1}] \\
 &= \frac{[Q_q]}{\epsilon} \{ f(\lambda_q)P(\lambda_q)(\lambda_q + \epsilon I - [u]) - f(\lambda_q + \epsilon)P(\lambda_q + \epsilon) \\
 & \quad \times (\lambda_q I - [u]) \} \\
 &= [Q_q] \{ f(\lambda_q)P(\lambda_q)I - (f(\lambda_q)P'(\lambda_q) + f'(\lambda_q)P(\lambda_q))(\lambda_q I - [u]) \} \\
 & \quad \dots \quad (73)
 \end{aligned}$$

in the limit.

Now suppose that $f([u]) = [u]^m$. Then (73) becomes

$$\begin{aligned}
 & f(\lambda_q)[Z_q] + f(\lambda_{q+1})[Z_{q+1}] \\
 &= \lambda_q^m [Q_q] \left\{ P(\lambda_q)I - \left(P'(\lambda_q) + \frac{m}{\lambda_q} P(\lambda_q) \right) (\lambda_q I - [u]) \right\}. \quad (74)
 \end{aligned}$$

It is now clear that if λ_1 is not one of the repeated roots, then the first term in the expansion (57) is still the dominant one when m is large. Hence the method of successive substitution yields the fundamental mode and frequency exactly as before. When, however, λ_1 is a repeated root, the matter is not quite so simple. The pair of terms (74) (with $q=1$) are dominant, but the multiplier of λ_1^m is now a function of m . If m were very large indeed, the expression on the right of (74) could be replaced by

$$-m\lambda_1^{m-1}P(\lambda_1)(\lambda_1 I - [u])[Q_1]. \quad \dots \quad (75)$$

Thus in the limit when $m \rightarrow \infty$, the ratio of corresponding elements in the matrices $[u]^{m+1}$ and $[u]^m$ would yield λ_1 . Further, the matrix in (75), when multiplied by $(\lambda_1 I - [u])$, is zero by the Cayley-Hamilton theorem, and it is therefore of the form (66). Accordingly, even in this case, the method of successive substitution, if carried far enough, will yield the fundamental frequency and a possible fundamental mode. This can hardly be considered a practical method of solution on account of the slowness of the convergence, but a modified method enables this difficulty to be overcome. Take an arbitrary element of the matrix, and let its values in successive substitutions be Φ_m, Φ_{m+1} , etc. Then, if m is large enough for

the first pair of terms in (57) to have become dominant, it follows from (74) that

$$\left. \begin{aligned} \Phi_m &= \lambda_1^m (A + mB), \\ \Phi_{m+1} &= \lambda_1^{m+1} (A + m + 1B), \text{ etc.} \end{aligned} \right\} \dots \quad (76)$$

The set of equations (76) can be solved for λ_1 and B without much difficulty, and the form of the matrix as $m \rightarrow \infty$ can therefore be found.

Cases where a root is repeated more than once can be discussed on similar lines to the foregoing, but the matter will not be pursued here. The results of the discussion on repeated roots can be summarized in the statement that a repetition of a root other than the fundamental does not affect the application of the method, but that, if the fundamental root is repeated, special methods are required.

§ 7. Determination of the Overtones.

Let $[\phi]_0$ be an arbitrary amplitude matrix. Then by equation (62)

$$[D]^m [\phi]_0 = \sum_{r=1}^{r=n} \lambda_r^m [Z_r] [\phi]_0 \dots \quad (77)$$

Also (see equation (58))

$$[Z_r](\lambda_r I - [u]) = 0 \dots \quad (78)$$

by the Cayley-Hamilton theorem. Thus by Theorem II. of Appendix I.

$$[Z_r] = \begin{bmatrix} \alpha_{1r} A_{1r} & \alpha_{1r} A_{2r} & \dots & \alpha_{1r} A_{nr} \\ \alpha_{2r} A_{1r} & \alpha_{2r} A_{2r} & \dots & \alpha_{2r} A_{nr} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \alpha_{nr} A_{1r} & \alpha_{nr} A_{2r} & \dots & \alpha_{nr} A_{nr} \end{bmatrix}, \quad (79)$$

and by the argument used at the end of § 5 it follows that the coefficients $\alpha_{r,r}$ are proportional * to the amplitude in the mode which corresponds to the latent root λ_r . Hence

$$[Z_r][\phi]_0 = R_r[\alpha_r], \quad \dots \quad (80)$$

where

$$R_r = A_{1r}\phi_1 + A_{2r}\phi_2 + \dots + A_{nr}\phi_n. \quad \dots \quad (81)$$

* For the sake of definiteness the absolute values may be fixed by some arbitrary rule, e.g., $\sum_p \alpha_{pr} = n$. The rule also fixes the absolute values of the coefficients A.

Finally,

$$[D]^m[\phi]_0 = \sum_{r=1}^{r=n} \lambda_r^m R_r[\alpha_r]. \quad \dots \quad (82)$$

Now suppose that m is a large number. Then, since $\lambda_1 > \lambda_2 > \lambda_3 > \dots > \lambda_n$, the dominant term on the right of (82) will be the first for which the coefficient R_r is not zero *. For example, when R_1 is not zero, the first or fundamental term is dominant.

It is now clear that the overtones can be obtained by the method of successive substitution when the coefficients A appropriate to the fundamental, first overtone, etc., are known. But their values for the fundamental mode can be obtained in the manner explained at the end of § 5. To find the first overtone it is only necessary to choose the initial amplitudes $[\phi]_0$ so that R_1 shall vanish, and carry out the successive substitutions in the usual way. While it is thus theoretically possible to obtain the frequency and amplitude ratios of the first overtone by successive substitution in the dynamical matrix, yet the process has practical drawbacks which seriously impair its usefulness. For it must be remembered that the coefficients A will in practice never be known with absolute accuracy, so that, in fact, the fundamental will not be completely absent from the selected initial mode. Thus when the substitution is repeated many times the fundamental will appear more and more strongly until the overtone is ultimately completely masked. For example, suppose that the relative amplitude of the fundamental in the initial mode is 10^{-6} and that $\lambda_1 = 3\lambda_2$ †. Then after thirteen substitutions the relative amplitude is approximately unity. Evidently, then, the fundamental must be determined very accurately if it is desired to obtain the first overtone by successive substitution, and the number of these substitutions must be great enough to ensure that the second overtone has become insignificant, but not large enough to make the fundamental important ‡.

* The variables R_r are evidently normal coordinates for the system.

† This implies that the frequency of the first overtone is $\sqrt{3}$ times that of the fundamental. This ratio is commonly much larger, and then the fundamental becomes dominant even sooner than in the example given.

‡ A better variation of this scheme is to modify the amplitude ratios at each stage of the substitution so as to satisfy the equation $R_1 = 0$ (see equation (81)).

The method just described is simple in theory, but it cannot be considered very practical, and it only applies to the first overtone. There is, however, a general method for obtaining the overtones in succession which will now be explained. This method is based on the fact that in any free motion from which the fundamental oscillation is absent the equation

$$A_{11}\phi_1 + A_{21}\phi_2 + \dots + A_{n1}\phi_n = 0 \quad \dots \quad (83)$$

is satisfied *at all instants*. Hence one of the dynamical coordinates can be eliminated, and the corresponding equation of motion can be discarded as redundant. Then the $(n-1)$ modified equations of motion are appropriate to a dynamical system which possesses all the modes of oscillation of the original system with the exception of the fundamental. The fundamental of the modified system (*i. e.*, the first overtone of the original system) can be found by the method of successive substitution in the ordinary way; and the values of the modified coefficients A which are required in the determination of the *second* overtone can be obtained by the method given at the end of § 5.

Suppose for convenience that the coordinate ϕ_n is selected for elimination, and let equation (83) be equivalent to

$$-\phi_n = \beta_{11}\phi_1 + \beta_{21}\phi_2 + \dots + \beta_{n-1,1}\phi_{n-1}. \quad \dots \quad (84)$$

Then on substitution in the first $(n-1)$ of the dynamical equations summarized in the matrix equation (55) they become

$$\left. \begin{aligned} -\phi_1 &= (D_{11} - \beta_{11}D_{1n})\ddot{\phi}_1 + (D_{12} - \beta_{21}D_{1n})\ddot{\phi}_2 + \dots \\ &\quad \dots + (D_{1,n-1} - \beta_{n-1,1}D_{1n})\ddot{\phi}_{n-1}, \\ -\phi_2 &= (D_{21} - \beta_{11}D_{2n})\ddot{\phi}_1 + (D_{22} - \beta_{21}D_{2n})\ddot{\phi}_2 + \dots \\ &\quad \dots + (D_{2,n-1} - \beta_{n-1,1}D_{2n})\ddot{\phi}_{n-1}, \\ \dots &\quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \\ -\phi_{n-1} &= (D_{n-1,1} - \beta_{11}D_{n-1,n})\ddot{\phi}_1 + (D_{n-1,2} - \beta_{21}D_{n-1,n})\ddot{\phi}_2 + \dots \\ &\quad \dots + (D_{n-1,n-1} - \beta_{n-1,1}D_{n-1,n})\ddot{\phi}_{n-1}. \end{aligned} \right\} \quad \dots \quad (85)$$

These are equivalent to the matrix equation

$$[\phi] = -[D'][\phi], \quad \dots \quad (86)$$

where $[D']$ is a modified dynamical matrix of order $(n-1)$ whose elements are given by

$$D'_{rs} = D_{rs} - \beta_{s1} D_{rn} \quad \dots \quad (87)$$

The first overtone can now be obtained from (86) just as the fundamental was obtained from (55), and the second and higher overtones can obviously be determined by a continuation of the process. At each stage the order of the dynamical matrix is reduced by 1, and it is evident that the process is free from the arithmetical errors inherent in the method first discussed in this section.

If it should happen that interest is confined to the oscillations of the highest frequency, yet another modification of the procedure is advantageous. Equation (56) can be written in the alternative form

$$[\phi] = \frac{1}{p^2} [D]^{-1} [\phi]. \quad \dots \quad (88)$$

It follows at once from the theory given in §5 that the most rapid oscillation will be obtained when $[D]^{-1}$ is used in place of $[D]$, and the other modes can be obtained in order of decreasing frequency by the method just explained.

By way of example, these methods for obtaining the overtones will be applied to the triple pendulum discussed in §2. From the expression (29) for $[D]^9$ it follows that the fundamental mode is absent * when

$$967500 x_1 + 2217618 x_2 + 3795822 x_3 = 0,$$

or when

$$-x_3 = 0.254885 x_1 + 0.584226 x_2. \quad \dots \quad (89)$$

Hence, by equations (25) and (87),

$$\begin{aligned} [D'] &= \frac{l}{6g} \begin{bmatrix} 2 - 2 \times 0.254885 & 2 - 2 \times 0.584226 \\ 2 - 5 \times 0.254885 & 5 - 5 \times 0.584226 \end{bmatrix} \\ &= \frac{l}{6g} \begin{bmatrix} 1.490230 & 0.831548 \\ 0.725575 & 2.078870 \end{bmatrix}. \quad \dots \quad (90) \end{aligned}$$

* If the dynamical matrix is symmetrical, as in the present example, the coefficients in this equation are proportional to the amplitudes in the corresponding degrees of freedom for the fundamental.

By repeated squaring it is found that

$$[D']^{16} = \left(\frac{l}{6g} \right)^{16} \begin{bmatrix} 1545447.5 & 2396137.2 \\ 2090771.9 & 3241636.1 \end{bmatrix}, \quad \dots \quad (91)$$

and one further multiplication by $[D']$ gives

$$[D']^{17} = \left(\frac{l}{6g} \right)^{17} \begin{bmatrix} 4041649.5 & 6266371.5 \\ 5467781.1 & 8477517.2 \end{bmatrix}, \quad \dots \quad (92)$$

The ratio of corresponding elements in the numerical matrices is 2.615197. Hence (see § 2) this is the value of ω for the first overtone. Also the ratios of the amplitudes in the first overtone are

$$\frac{x_2}{x_1} = \frac{5467781.1}{4041649.5} = \frac{8477517.2}{6266371.5} = 1.352859, \quad \dots \quad (93)$$

and by equation (89)

$$\frac{x_3}{x_1} = -1.045260. \quad \dots \quad \dots \quad \dots \quad (94)$$

The first overtone will be absent if

$$4041649.5 x_1 + 6266371.5 x_2 = 0,$$

or, if

$$\frac{x_2}{x_1} = -0.644974. \quad \dots \quad \dots \quad \dots \quad (95)$$

This equation therefore holds for the second overtone, and since (89) must also be satisfied it follows that

$$\frac{x_3}{x_1} = +0.121926. \quad \dots \quad \dots \quad \dots \quad (96)$$

In order to find the value of ω for the second overtone it is only necessary to substitute the known mode in the dynamical equation (26). Hence $\omega = 0.953903$.

The second overtone can also be obtained directly from the inverse of the dynamical matrix. It is easily shown that

$$[D]^{-1} = \frac{g}{l} \begin{pmatrix} 5 & -2 & 0 \\ -2 & 3 & -1 \\ 0 & -1 & 1 \end{pmatrix}. \quad \dots \quad \dots \quad (97)$$

$$\text{Let } \varpi' = \frac{p^2 l}{q} = \frac{6}{\varpi} \dots \dots \dots \quad (98)$$

Then if the initially assumed amplitudes are equal, it is found after fifteen successive substitutions in the usual way that

$$\frac{x_2}{x_1} = -0.644972$$

and

$$\frac{x_3}{x_1} = +0.121924.$$

Also $\varpi' = 6.289944$, so that by (98) $\varpi = 0.953904$.

§8. Approximate Treatment of Continuous Systems.

Problems on the oscillations of continuous systems can often be discussed approximately by supposing the system divided into a finite number of rigid units suitably inter-connected, or, more generally, by replacing the system by another having only a finite number of degrees of freedom *. But if the approximation is to be good, the number of degrees of freedom must usually be large, and the solution of the dynamical equations by orthodox methods becomes so laborious as to be impracticable. In many cases, however, a solution can be obtained with comparatively little labour by the method explained in this paper. (The restrictions on the applicability of the method have already been indicated.) A few examples will now be given, and, as the problems selected for discussion all have known exact solutions, the accuracy of the approximations obtained can be tested.

When it is desired to obtain a highly accurate solution for a continuous system, so that it is necessary to divide the system into a large number of elements, it becomes important to choose an initial mode which is nearly correct in order to save labour. Such a mode can be derived from a preliminary calculation with the system divided into a smaller number of elements. However, in the examples which follow, an inaccurate initial mode has deliberately been chosen in order that the convergence of the solution may be clearly exhibited.

* The deformable bodies of the actual system are replaced by ideal bodies whose displacements are governed by inexorable laws. Such ideal bodies have been called "semi-rigid," and they must be regarded as generalized mechanisms.

§ 9. Example A : Torsional Oscillation of a Uniform Cantilever.

It will be supposed that the cantilever beam considered is of cylindrical form, with a section having a pair of perpendicular axes of symmetry, and composed of isotropic elastic material ; also the support at the root will be assumed rigid. Clearly the flexural and torsional oscillations of such a beam are uncoupled, and attention will here be confined to the torsional oscillations.

Let s be the span of the beam, C the torsional elastic stiffness (torque per radian of twist) of unit length, and P the moment of inertia of unit length about the line of centroids. Suppose the beam cut into, say, ten equal sections, and let these be rigid and connected to their neighbours by torsion springs so arranged that the torsional stiffness measured at the *middle* of each section is the same as that for the corresponding position in the continuous beam. This system has ten degrees of freedom, and the fundamental mode and frequency will be obtained by the method of this paper.

The flexibility matrix is very easily obtained. For if unit couple be applied at the distance y_1 from the root, then the twist θ at any section distant y from the root is y/C if $y < y_1$, and y_1/C if $y > y_1$. Hence the flexibility matrix is

$$[f] = \begin{pmatrix} s \\ C \end{pmatrix} \times \begin{pmatrix} 0.05 & 0.05 & 0.05 & 0.05 & 0.05 & 0.05 & 0.05 & 0.05 & 0.05 & 0.05 \\ 0.05 & 0.15 & 0.15 & 0.15 & 0.15 & 0.15 & 0.15 & 0.15 & 0.15 & 0.15 \\ 0.05 & 0.15 & 0.25 & 0.25 & 0.25 & 0.25 & 0.25 & 0.25 & 0.25 & 0.25 \\ 0.05 & 0.15 & 0.25 & 0.35 & 0.35 & 0.35 & 0.35 & 0.35 & 0.35 & 0.35 \\ 0.05 & 0.15 & 0.25 & 0.35 & 0.45 & 0.45 & 0.45 & 0.45 & 0.45 & 0.45 \\ 0.05 & 0.15 & 0.25 & 0.35 & 0.45 & 0.55 & 0.55 & 0.55 & 0.55 & 0.55 \\ 0.05 & 0.15 & 0.25 & 0.35 & 0.45 & 0.55 & 0.65 & 0.65 & 0.65 & 0.65 \\ 0.05 & 0.15 & 0.25 & 0.35 & 0.45 & 0.55 & 0.65 & 0.75 & 0.75 & 0.75 \\ 0.05 & 0.15 & 0.25 & 0.35 & 0.45 & 0.55 & 0.65 & 0.75 & 0.85 & 0.85 \\ 0.05 & 0.15 & 0.25 & 0.35 & 0.45 & 0.55 & 0.65 & 0.75 & 0.85 & 0.95 \end{pmatrix} \quad \dots \quad (99)$$

Also the moment of inertia of any one of the slices is $0.1 sP$. Hence the dynamical matrix is simply

$$[D] = \frac{0.1 s^2 P}{C} [d], \dots \quad (100)$$

where $[d]$ is the numerical matrix in (99). Let $p = 2\pi f$, and let $[\theta]$ be the amplitude matrix. Then

$$\varpi [\theta] = [d] [\theta], \dots \quad (101)$$

where

$$\varpi = \frac{10C}{s^2 p^2 P} \dots \quad (102)$$

The process of solution of (101) by the method of successive substitution is shown concisely in Table III., where the arbitrary initial mode is linear. The first column under each heading gives the results of the substitution of the amplitudes given in the column immediately on the left, and the second column gives the new amplitude ratios with the amplitude at 0.95 of the span taken as unity.

The differential equation governing the oscillations of the continuous beam is

$$P\ddot{s} - \frac{\partial}{\partial y} \left(C \frac{\partial s}{\partial y} \right) = 0, \dots \quad (103)$$

and the end conditions are:—

$$s = 0 \quad \text{when} \quad y = 0, \dots \quad (104)$$

$$C \frac{\partial s}{\partial y} = 0 \quad \text{when} \quad y = s. \dots \quad (105)$$

Now when the beam is oscillating in one mode only

$$s = \theta \sin pt,$$

and by equations (103) and (104)

$$\theta = \theta_1 \sin p \sqrt{\frac{P}{C}} y. \dots \quad (106)$$

Hence for the fundamental mode, by (105),

$$p = \frac{\pi}{2s} \sqrt{\frac{C}{P}}, \dots \quad (107)$$

so that

$$\varpi = \frac{40}{\pi^2} = 4.053. \dots \quad (108)$$

TABLE III.
 Fundamental Torsional Oscillation of a Uniform Cantilever.

Initial mode.	First approximation.		Second approximation.		Third approximation.		Fourth approximation.		Exact solution for continuous beam.
	0.25	0.0752	0.3139	0.0783	0.3190	0.0786	0.3196	0.0787	
0.05	0.745	0.2241	0.9342	0.2330	0.9492	0.2340	0.9508	0.2342	0.2342
0.15	1.225	0.3684	1.5321	0.3821	1.5562	0.3837	1.5587	0.3839	0.3839
0.25	1.68	0.5053	2.0932	0.5220	2.1249	0.5239	2.1281	0.5241	0.5241
0.35	2.10	0.6316	2.6037	0.6493	2.6414	0.6512	2.6452	0.6514	0.6515
0.45	2.475	0.7444	3.0511	0.7609	3.0930	0.7626	3.0972	0.7627	0.7628
0.55	2.795	0.8406	3.4240	0.8539	3.4685	0.8551	3.4729	0.8553	0.8553
0.75	3.05	0.9173	3.7129	0.9259	3.7586	0.9267	3.7631	0.9267	0.9267
0.85	3.23	0.9714	3.9100	0.9751	3.9561	0.9753	3.9606	0.9754	0.9754
0.95	3.325	1.0	4.0100	1.0	4.0561	1.0	4.0606	1.0	1.0
$\overline{w} = 3.50$		4.010		4.056		4.061		4.053	

Also if θ_1 is chosen so that the amplitude is unity at 0.95 of the span, then (106) becomes

$$\theta = 1.00309 \sin\left(\frac{\pi y}{2s}\right) \quad \dots \quad \dots \quad \dots \quad (109)$$

The true mode for the continuous beam has been calculated from this equation, and the results are entered in the last column of Table III. The error in the mode (at the centres of the sections of the sliced beam) does not exceed 1 part in 10^4 , while the error in the fundamental frequency is 1 part in 10^3 .

§ 10. Example B : Flexural Oscillation of a Tapered Beam resembling an Airscrew Blade.

As explained in Appendix II., a simple method has been found for specifying the inertial and elastic characteristics of cantilever beams which are such that the differential equations governing the flexural oscillations have known exact solutions. It is not difficult to devise tapered beams of this kind which very closely resemble an (untwisted) airscrew blade. The matrix method of solution will now be applied to a particular example of this class of beam.

The following symbols will be used :—

B =flexural rigidity at a current point,

A =sectional area at a current point,

σ =density of the material of the beam (constant),

z =amplitude of oscillation.

Also the suffices 0 and 1 will be used to designate quantities measured at the root and tip respectively. The particular beam which will be studied has the specification

$$A = A_0 (1 - \eta), \quad \dots \quad (110)$$

$$B = B_0 \frac{(1 - \eta)^2 (184 + 258\eta + 222\eta^2 + 76\eta^3 - 75\eta^4)}{184 (1 + 15\eta)}, \quad (111)$$

where

$$\eta = \frac{y}{s} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (112)$$

and s is the span. It is shown in Appendix II. that the

fundamental mode and frequency of this beam are given by

$$z = \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} (6\eta^2 + 28\eta^3 - 15\eta^4), \dots \quad (113)$$

and

$$p^2 = 13.6956 \left(\frac{B_0}{s^4 \sigma A_0} \right) \dots \quad (114)$$

In the approximate treatment of the oscillations of this beam by the matrix method, the beam will be supposed divided into ten slices of equal length. Each of these slices should be represented by a particle situated at the centroid, but the centroid is very near the middle of the slice, except in the case of the two highly tapered slices next the tip. Accordingly the particles will be supposed situated at the following fractions of the span:—0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.84, 0.93. The mass of each particle is equal to that of the corresponding slice of the beam, and is immediately calculable from equation (110).

The flexibility coefficients must now be obtained. These form a symmetrical matrix, and it is therefore sufficient to consider the case where the load is external to the point at which the displacement is measured. Let unit load be applied at a distance Hs from the root. Then the bending-moment at a current point distant ηs from the root is

$$M = s(H - \eta'),$$

and the curvature at this point is

$$R = \frac{1}{B_{\eta'}} = \frac{s(H - \eta')}{B_{\eta'}} \dots \quad (115)$$

The bending of an element of length $sd\eta'$ causes a rotation of the part of the beam external to the element of amount

$$d\phi = \frac{sd\eta'}{R} = \frac{s^2(H - \eta')d\eta'}{B_{\eta'}},$$

and the consequent displacement of an external point situated at a distance $s\eta$ from the root is

$$dz = \frac{s^3(H - \eta')(\eta - \eta')d\eta}{B_{\eta'}}.$$

Hence the total displacement is

$$z = \int_0^\eta \frac{s^3(H-\eta')(\eta-\eta')d\eta'}{B_{\eta'}} \quad \dots \quad (116)$$

The values of the flexibility coefficients were obtained from this formula by the aid of Simpson's rule.

The final expression for the dynamical matrix of the sliced beam is

$$[D] = \frac{s^4 \sigma A_0}{10^3 P_0} [d], \quad \dots \quad (117)$$

where $[d]$ is the numerical matrix given in equation (118). Hence the matrix equation giving the mode and frequency is

$$\omega[z] = [d][z], \quad \dots \quad (119)$$

$$\text{where } \omega = \frac{10^3 B_0}{\sigma p^2 s^4 A_0} \quad \dots \quad (120)$$

The solution of (119) by successive substitution is shown in Table IV., where the arbitrary initial mode is parabolic. Since the amplitude very near the tip is liable to rather larger errors than elsewhere for highly tapered beams, the amplitude at 0.75 of the span has been arbitrarily adopted as the standard of reference. It will be seen that the error in the frequency is less than 0.5 per cent., and the errors in the mode are of the same order.

$[d] =$

0.0048	0.0179	0.0278	0.0338	0.0374	0.0378	0.0350	0.0290	0.0195	0.0072
0.0200	0.1539	0.2895	0.3848	0.4383	0.4504	0.4224	0.3530	0.2396	0.0890
0.0351	0.3281	0.8018	1.1895	1.4256	1.5089	1.4399	1.2190	0.8340	0.3122
0.0494	0.5032	1.3725	2.3550	3.0453	3.3530	3.2778	2.8195	1.9500	0.7361
0.0646	0.6774	1.9440	3.5990	5.1304	5.9868	6.0473	5.3138	3.7247	1.4204
0.0798	0.8509	2.5148	4.8431	7.3172	9.1962	9.7464	8.8148	6.2893	2.4299
0.0950	1.0260	3.0855	6.0872	9.5029	12.5311	14.1421	13.3540	9.7689	3.8417
0.1102	1.2002	3.6570	7.3307	11.6902	15.8666	18.6956	18.7320	14.2533	5.7557
0.1235	1.3574	4.1700	8.4500	13.6570	18.8680	22.7941	23.7555	19.0581	8.0196
0.1368	1.5139	4.6838	9.5700	15.6250	21.8691	26.8919	28.7782	24.0587	10.8837

• . . . (118)

TABLE IV.

Fundamental Flexural Oscillation of a Tapered Beam.

η .	Arbitrary initial mode.	First approximation.	Second approximation.	Third approximation.	Fourth approximation.	Fifth approximation.	Exact solution for continuous beam.
0.05	0.004	0.1358	0.00183	0.1288	0.00177	0.1284	0.00177
0.15	0.040	1.5916	0.02143	1.5502	0.02142	1.5458	0.02138
0.25	0.111	5.5129	0.07420	5.2631	0.07271	5.2493	0.07260
0.35	0.217	12.4446	0.16749	11.9308	0.16481	11.9025	0.16460
0.45	0.360	22.8059	0.30696	21.9603	0.30325	21.9144	0.30307
0.55	0.537	36.7092	0.49410	35.5004	0.49037	35.4370	0.49007
0.65	0.751	54.0074	0.72692	52.4388	0.72436	52.3618	0.72413
0.75	1.0000	74.2962	1.00000	72.3938	1.00000	72.3097	1.00000
0.84	1.2544	94.5355	1.27243	92.3589	1.27578	92.2751	1.27610
0.93	1.5376	115.9423	1.56055	113.5088	1.56794	113.4305	1.56868
ϖ		74.296		72.394		72.310	

§11. *Example C : Torsional Oscillation of a Tapered Beam resembling an Airscrew Blade.*

A method is given in Appendix III. for determining the properties of beams having a known mode of torsional oscillation. In particular it is shown that a beam whose polar moment of inertia and torsional stiffness are given by the expressions

$$P = P_0(1-\eta)^2, \quad \dots \quad \dots \quad \dots \quad \dots \quad (121)$$

$$C = C_0 \frac{(1-\eta)^2(42 + 126\eta + 237\eta^2 - 200\eta^3)}{42(1 + 120\eta)} \quad \dots \quad (122)$$

has a fundamental mode and frequency given by

$$\theta = \left(\frac{\theta_1}{41} \right) (2\eta + 119\eta^2 - 80\eta^3), \quad \dots \quad \dots \quad \dots \quad \dots \quad (123)$$

and

$$p^2 = \frac{5}{7} \left(\frac{C_0}{s^2 P_0} \right) \quad \dots \quad \dots \quad \dots \quad \dots \quad (124)$$

The torsional flexibility coefficients are very readily obtained. Since the matrix is symmetrical, it is sufficient to take the case where the unit load is applied outside the point where the displacement is measured. Now the twist per unit length under unit couple is $1/C$, so that the total twist at a current point is

$$\theta = s \int_0^\eta \frac{d\eta'}{C_{\eta'}}. \quad \dots \quad \dots \quad \dots \quad \dots \quad (125)$$

In the approximate treatment by the matrix method the beam is supposed cut into twenty rigid pieces of equal length, and the effective centres of the segments will be assumed to be at their mid-points, except for the two nearest to the tip which will be assumed concentrated at points lying at 0.92 and 0.96 of the span. The inertias of the slices are obtained from (121) by integration, and the dynamical matrix constructed. The expression for this matrix is

$$[D] = \left(\frac{s^2 P_0}{2880 C_0} \right) [d], \quad \dots \quad \dots \quad \dots \quad \dots \quad (126)$$

$[d] =$

8.43	7.59	6.79	6.04	5.33	4.66	4.04	3.47	2.93	2.45	2.00	1.60	1.25	0.938	0.672	0.451	0.273	0.140	0.0517	0.0074
48.65	43.44	38.62	34.08	29.83	25.86	22.17	18.77	15.65	12.81	10.26	7.99	6.003	4.302	2.883	1.749	0.898	0.331	0.0473	
108.86	96.77	85.40	74.74	64.79	55.55	47.02	39.21	32.10	25.70	20.02	15.04	10.78	7.23	4.383	2.251	0.829	0.118		
179.4	158.3	138.5	120.1	103.0	87.16	72.67	59.50	47.64	37.10	27.88	19.98	13.39	8.123	4.171	1.537	0.220			
252.9	221.3	191.8	164.5	139.2	116.1	95.05	76.11	59.28	44.54	31.92	21.40	12.98	6.664	2.455	0.351				
324.3	281.1	241.0	204.0	170.1	139.3	111.5	86.85	65.27	46.77	31.35	19.02	9.764	3.597	0.514					
390.0	334.4	283.0	236.0	193.2	154.7	120.5	90.54	64.88	43.49	26.38	13.55	4.991	0.713						
447.4	378.7	315.8	258.5	207.0	161.2	121.2	86.82	58.20	35.30	18.13	6.678	0.954							
494.9	412.6	337.8	270.5	210.7	158.3	113.4	76.04	46.12	23.68	8.725	1.246								
530.9	434.7	348.0	271.1	203.7	146.0	97.84	59.34	30.47	11.23	1.604									
554.7	444.1	345.9	259.9	186.2	124.8	75.73	38.89	14.33	2.047										
565.4	440.3	330.9	237.1	158.9	96.41	49.51	18.24	2.606											
562.5	422.7	302.9	203.0	123.2	63.24	23.30	3.329												
545.5	390.9	262.0	158.9	81.61	30.07	4.295													
513.7	344.3	208.9	107.3	39.51	5.645														
466.4	282.9	145.3	53.52	7.646															
402.7	206.8	76.18	10.88																
321.2	118.3	16.91																	
208.7	29.81																		
		64.55																	

The blank spaces in a column are to be supposed filled with the last number appearing in the column. (127)

where $[d]$ is the numerical matrix given in equation (127), and the equation governing the oscillations is

$$\omega[\theta] = [d][\theta], \quad \dots \quad \dots \quad \dots \quad (128)$$

where

$$\omega = \frac{2880C_0}{s^2 p^2 P_0}. \quad \dots \quad \dots \quad \dots \quad (129)$$

The process of solution by successive substitution is give in Table V., where the assumed initial mode is linear. It will be seen that the error in the frequency is about 1 part in 400. Over the greater part of the span the error in the mode is of the order of 1 part in 500, but quite near the tip the error is somewhat larger.

APPENDIX I.

Two Theorems on Matrices.

Theorem I.

Let $f([u])$ be any polynomial of the square matrix $[u]$, whose latent roots are $\lambda_1, \lambda_2, \dots, \lambda_n$. Then

$$f([u]) = \sum_{r=1}^{r=n} f(\lambda_r) [Z_r],$$

where

$$[Z_r] = \frac{\prod_{s \neq r} (\lambda_s I - [u])}{\prod_{s \neq r} (\lambda_s - \lambda_r)}$$

Let the characteristic equation of $[u]$ be

$$\lambda^n + p_1 \lambda^{n-1} + p_2 \lambda^{n-2} + \dots + p_n = 0. \quad \dots \quad (1)$$

Then, by the Cayley-Hamilton theorem, $[u]$ satisfies the equation

$$[u]^n + p_1 [u]^{n-1} + p_2 [u]^{n-2} + \dots + p_n I = 0, \quad \dots \quad (2)$$

where I is the unit matrix of order n . By equation (1) λ^n is linearly expressible in terms of unity and the first $(n-1)$ powers of λ . On multiplication by λ , and substitution of the known expression for λ^n , an expression of degree $(n-1)$ for λ^{n+1} is obtained. In the same way all the higher powers of λ can be expressed as polynomials of degree $(n-1)$, and therefore an arbitrary polynomial $f(\lambda)$

TABLE I
Fundamental Torsional Oscillations

Initial mode.	First approximation.		Second approximation.		Third approximation.		approx.
	Value	Error	Value	Error	Value	Error	
0.04	23.70	0.0054	18.65	0.0045	17.85	0.0044	17.6
0.12	149.83	0.0339	119.25	0.0289	114.04	0.0280	112.9
0.20	366.13	0.0828	295.88	0.0716	283.58	0.0696	280.7
0.28	654.81	0.1481	539.30	0.1305	517.74	0.1271	512.7
0.36	999.34	0.2260	839.25	0.2031	807.58	0.1983	800.1
0.44	1385.59	0.3134	1185.81	0.2870	1144.24	0.2810	1134.3
0.52	1801.46	0.4074	1569.17	0.3798	1518.83	0.3730	1512.1
0.60	2236.49	0.5058	1979.69	0.4791	1922.38	0.4721	1908.3
0.68	2682.15	0.6066	2408.51	0.5829	2346.38	0.5762	2331.0
0.76	3130.23	0.7079	2846.44	0.6889	2781.79	0.6832	2763.4
0.84	3573.66	0.8082	3284.94	0.7951	3219.94	0.7908	3203.9
0.92	4006.45	0.9061	3716.33	0.8995	3652.87	0.8971	3632.9
1.00	4421.81	1.0000	4131.63	1.0000	4071.78	1.0000	4057.7
1.08	4814.10	1.0887	4524.83	1.0952	4468.48	1.0974	4456.1
1.16	5176.54	1.1707	4886.44	1.1827	4834.67	1.1874	4824.3
1.24	5502.52	1.2444	5209.26	1.2608	5162.08	1.2678	5153.8
1.32	5785.08	1.3083	5485.84	1.3278	5442.84	1.3367	5436.6
1.40	6016.50	1.3606	5708.75	1.3817	5669.19	1.3923	5664.4
1.472	6169.38	1.3952	5853.03	1.4166	5815.68	1.4283	5812.4
1.536	6222.74	1.4073	5901.92	1.4285	5865.31	1.4405	5862.5

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LE V.

litation of a Tapered Beam.

ourth ximation.	Fifth approximation.		Sixth approximation.		Seventh approximation.		Exact solution for con- tinuous beam.
0.0044	17.63	0.0044	17.62	0.0044	17.62	0.0044	0.0044
0.0278	112.64	0.0278	112.56	0.0278	112.53	0.0278	0.0279
0.0692	280.13	0.0691	279.94	0.0691	279.87	0.0690	0.0693
0.1264	511.62	0.1262	511.28	0.1261	511.15	0.1261	0.1264
0.1972	798.43	0.1969	797.92	0.1968	797.73	0.1968	0.1973
0.2795	1132.02	0.2792	1131.32	0.2791	1131.21	0.2791	0.2796
0.3727	1503.81	0.3709	1502.92	0.3707	1502.60	0.3707	0.3713
0.4703	1904.91	0.4699	1904.02	0.4697	1903.65	0.4696	0.4704
0.5744	2327.15	0.5740	2326.31	0.5738	2325.92	0.5738	0.5745
0.6810	2761.61	0.6812	2760.90	0.6810	2760.49	0.6810	0.6817
0.7896	3199.75	0.7893	3199.17	0.7892	3198.77	0.7891	0.7897
0.8953	3633.49	0.8962	3633.14	0.8962	3632.75	0.8962	0.8966
1.0000	4054.10	1.0000	4053.88	1.0000	4053.52	1.0000	1.0000
1.0982	4453.09	1.0984	4453.05	1.0985	4452.74	1.0985	1.0980
1.1889	4821.95	1.1894	4822.13	1.1895	4821.86	1.1895	1.1883
1.2701	5152.18	1.2709	5152.60	1.2710	5152.38	1.2711	1.2689
1.3398	5435.68	1.3408	5436.31	1.3410	5436.15	1.3411	1.3376
1.3960	5664.42	1.3972	5665.27	1.3975	5665.15	1.3976	1.3922
1.4324	5812.55	1.4337	5813.53	1.4341	5813.45	1.4342	1.4277
1.4448	5862.74	1.4461	5863.77	1.4465	5863.70	1.4466	1.4471
57.8	4054.1		4053.9		4053.5		4032

of any degree can also be reduced to a polynomial of the $(n-1)$ th degree, say

$$f(\lambda) = P_1 \lambda^{n-1} + P_2 \lambda^{n-2} + \dots + P_n. \quad \dots \quad (3)$$

$$\text{Now let } F(x) \equiv P_1 x^{n-1} + P_2 x^{n-2} + \dots + P_n. \quad \dots \quad (4)$$

Then, whenever λ is a root of (1),

$$f(\lambda) = F(\lambda) \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

By an exactly parallel argument equation (2) leads to the result

$$f([u]) = F([u]), \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)$$

where it is to be understood that the "constant" terms in the two functions are multiplied by the unit matrix. For the algebra of expressions containing only a single matrix besides the unit matrix is formally identical with ordinary algebra in virtue of the equations $I^q = I$, and $I[u] = [u]I = [u]$. Hence also if $[v]$ is an arbitrary matrix, it follows from the Lagrange interpolation formula of ordinary algebra that

$$F([v]) \equiv \sum_{r=1}^{r=n} F(a_r) \frac{\prod (a_s I - [v])}{\prod_{s \neq r} (a_s - a_r)}, \quad \dots \quad \dots \quad \dots \quad (7)$$

where the n numbers a are distinct but otherwise arbitrary. Now suppose $a_r = \lambda_r$, and put $[v] = [u]$. Then, by equations (5) and (6) the last formula becomes

$$f([u]) = \sum_{r=1}^{r=n} f(\lambda_r) \frac{\prod (\lambda_s I - [u])}{\prod_{s \neq r} (\lambda_s - \lambda_r)}, \quad \dots \quad \dots \quad \dots \quad (8)$$

This theorem appears to be due to Sylvester. Its great usefulness lies in the fact that with its aid the laborious direct calculation of the coefficients P becomes unnecessary. Explicit expressions for these coefficients as ratios of alternants of the latent roots have been given by H. F. Baker in the Proceedings of the London Mathematical Society, vol. xxxv. p. 335.

If the product $[A][x]$ is zero, while $[A]$ is not a zero matrix, and the cofactors of the elements of the determinant $[x]$ are not all zero, then the elements in any row of $[A]$ are proportional to the corresponding elements of the top row of $[A]$.

Let

$$[A] \equiv \begin{bmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & \dots & A_{2n} \\ \dots & \dots & \dots & \dots \\ A_{n1} & A_{n2} & \dots & A_{nn} \end{bmatrix}, \quad \dots \quad (9)$$

and

$$[x] = \begin{bmatrix} x_{11} & x_{12} & \dots & x_{1n} \\ x_{21} & x_{22} & \dots & x_{2n} \\ \dots & \dots & \dots & \dots \\ x_n & x_{n2} & \dots & x_{nn} \end{bmatrix}. \quad \dots \quad (10)$$

The matrix equation

$$[A][x] = 0 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (11)$$

is equivalent to n^2 ordinary equations. In order that the elements in the top row of the product may vanish, the following set of n equations must be satisfied :—

$$\left. \begin{array}{l} A_{11}x_{11} + A_{12}x_{21} + \dots + A_{1n}x_{n1} = 0, \\ A_{11}x_{12} + A_{12}x_{22} + \dots + A_{1n}x_{n2} = 0, \\ \dots \quad \dots \quad \dots \quad \dots \\ A_{11}x_{1n} + A_{12}x_{2n} + \dots + A_{1n}x_{nn} = 0. \end{array} \right\} \quad \dots \quad (12)$$

In order that these may be compatible it is necessary that

$$\left| \begin{array}{cccc} x_{11} & x_{21} & \dots & x_{n1} \\ x_{12} & x_{22} & \dots & x_{n2} \\ \dots & \dots & \dots & \dots \\ x_{1n} & x_{2n} & \dots & x_{nn} \end{array} \right| = 0. \quad \dots \quad (13)$$

Then, provided that the cofactors of the elements of this determinant are not all zero, equations (12) uniquely determine the ratios of the n numbers $A_{11}, A_{12}, \dots, A_{1n}$. Next, since the elements of the second row of the product are all zero

$$\left. \begin{array}{l} A_{21}x_{11} + A_{22}x_{21} + \dots + A_{2n}x_{n1} = 0, \\ A_{21}x_{12} + A_{22}x_{22} + \dots + A_{2n}x_{n2} = 0, \\ \dots \quad \dots \quad \dots \quad \dots \\ A_{21}x_{1n} + A_{22}x_{2n} + \dots + A_{2n}x_{nn} = 0. \end{array} \right\} \quad \dots \quad (14)$$

These equations are the same as the set (12) with A_{21} $A_{22} \dots A_{2n}$ written in place of $A_{11} A_{12} \dots A_{1n}$. Hence

$$\frac{A_{21}}{A_{11}} = \frac{A_{22}}{A_{12}} = \dots = \frac{A_n}{A_{1n}} \dots \dots \dots \quad (15)$$

The proportionality of the elements in the other rows follows in the same way.

APPENDIX II.

The Construction of Cantilever Beams having a known Mode of Flexural Oscillation.

The differential equation of flexural motion is

$$m\zeta + \frac{\partial^2}{\partial y^2} \left(B \frac{\partial^2 \zeta}{\partial y^2} \right) = 0, \dots \dots \dots \quad (1)$$

where m is the mass per unit length, and B is the flexural rigidity. When the beam is oscillating in a single mode,

$$\zeta = z \sin pt, \dots \dots \dots \quad (2)$$

where z is a function of y only, and equation (1) becomes

$$\frac{d^2}{dy^2} \left(B \frac{dz^2}{dy^2} \right) = mp^2 z. \dots \dots \dots \quad (3)$$

For a cantilever of length s the end conditions are:—

$$\text{For } y = 0, \quad z = 0, \dots \dots \dots \quad (4)$$

and

$$\frac{dz}{dy} = 0. \dots \dots \dots \quad (5)$$

$$\text{For } y = s, \quad B \frac{d^2 z}{dy^2} = 0, \dots \dots \dots \quad (6)$$

and

$$\frac{d}{dy} \left(B \frac{dz}{dy} \right) = 0. \dots \dots \dots \quad (7)$$

Let σ be the constant density of the material of the beam, and A the area of the cross-section. Then

$$m = \sigma A, \dots \dots \dots \quad (8)$$

and it will be convenient to write

$$B = EA^2 \tau, \dots \dots \dots \quad (9)$$

where E is Young's Modulus, and τ is a non-dimensional quantity, which for sections of a constant general form is proportional to (thickness of section) \div (width of section).

Equation (5) now becomes

$$\frac{d^2}{dy^2} \left(A^2 \tau \frac{d^2 z}{dy^2} \right) = \frac{\sigma p^2}{E} A z. \quad \dots \quad (10)$$

In outline the method consists in assigning a mode which is consistent with (4) and (5), and determining τ from equation (10) twice integrated. The constants of integration must be chosen to satisfy (6) and (7). When, however, it is desired to construct a beam which tapers to zero at the tip, the matter requires a rather more detailed examination.

Suppose that

$$\left. \begin{aligned} A &= (s-y)^l a(y), \\ \tau &= (s-y)^n t(y), \\ \frac{d^2 z}{dy^2} &= (s-y)^q d(y), \end{aligned} \right\} \quad \dots \quad (11)$$

where $a(s)$, $t(s)$, and $d(s)$ are neither zero nor infinite. Then the left-hand side of (10) contains the factor $(s-y)^{2l+n+q-2}$, and the right-hand side contains the factor $(s-y)^l$, for z does not vanish at the tip. Hence

$$2l+n+q-2=l,$$

or

$$n+q=(2-l). \quad \dots \quad (12)$$

Further, (6) and (7) will not be satisfied unless

$$2l+n+q>1, \quad \dots \quad (13)$$

which by (12) is equivalent to

$$l>-1. \quad \dots \quad (14)$$

Consider, now, the case where the shape of the section remains normal (not infinitely thin either horizontally or vertically) near the tip, so that $n=0$. Further, let the plan form at the tip be parabolic. Then $l=1$, and equation (12) gives $q=1$. Accordingly

$$A=(s-y)a(y), \quad \dots \quad (15)$$

and

$$\frac{d^2 z}{dy^2}=(s-y)d(y). \quad \dots \quad (16)$$

Example.—As a simple case let

$$A = a(s-y) \quad \dots \dots \dots \dots \dots \quad (17)$$

and

$$\frac{d^2z}{dy^2} = b(s+ry)(s-y). \quad \dots \dots \dots \quad (18)$$

By (4), (5), and (18) the mode of oscillation is given by

$$z = \frac{b}{12} \{6s^2y^2 + 2s(r-1)y^3 - ry^4\}. \quad \dots \dots \quad (19)$$

The differential equation (10) now becomes

$$\begin{aligned} \frac{d^2}{dy^2} \{ (s-y)^3(s+ry)\tau \} \\ = \left(\frac{\sigma p^2}{12aE} \right) (s-y) \{ 6s^2y^2 + 2s(r-1)y^3 - ry^4 \}. \end{aligned} \quad (20)$$

Since τ is to be finite at the tip, the two constants which appear when (20) is integrated must be chosen so that $(s-y)^3$ is a factor of the right-hand side. Hence it is found that

$$\tau = \frac{K}{s+ry} \left\{ \begin{aligned} (9r+49)s^4 + (13r+63)s^3y \\ + (12r+42)s^2y^2 + (6r-14)sy^3 - 5ry^4 \end{aligned} \right\}, \quad (21)$$

where

$$K = \frac{\sigma p^2}{5.6.7.12aE}. \quad \dots \dots \dots \quad (22)$$

When $y=0$, equation (21) gives

$$\tau_0 = (9r+49)s^3K, \quad \dots \dots \dots \quad (23)$$

and by (17)

$$A_0 = as. \quad \dots \dots \dots \quad (24)$$

Hence (22) becomes

$$\begin{aligned} p^2 &= \frac{2520}{(9r+49)} \left(\frac{EA_0\tau_0}{s^4\sigma} \right)^{\frac{1}{2}} \\ &= \frac{2520}{(9r+49)} \left(\frac{B_0}{s^4\sigma A_0} \right)^{\frac{1}{2}}, \end{aligned} \quad \dots \dots \dots \quad (25)$$

by equation (9).

It is found by trial that when $r=15$, the cantilever whose properties are given by (17) and (21) approximates

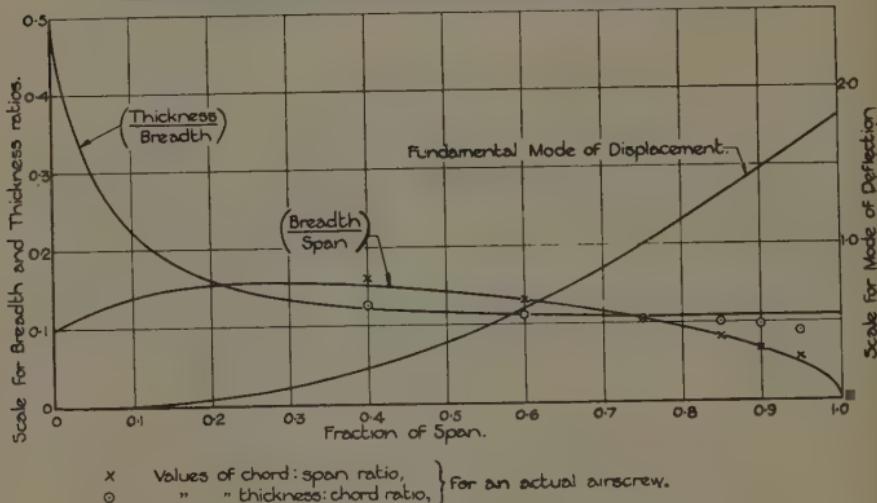
very closely to some airscrew blades at present in use. This is evident from fig. 2, where the ratios (width of section) \div (span) and (depth of section) \div (width of section) for a selected blade of the theoretical family are compared with the corresponding ratios for an actual duralumin airscrew.

Let

$$\eta = \left(\frac{y}{s} \right) \dots \dots \dots \dots \quad (26)$$

Fig. 2.

CHARACTERISTICS OF A TAPERED BEAM RESEMBLING AN AIRSCREW BLADE. (EXAMPLE B; FLEXURAL OSCILLATION). FIG 2.



Then the formulæ for the case $r=15$ can be conveniently written

$$A = A_0(1-\eta), \dots \dots \dots \dots \dots \dots \quad (27)$$

$$B = B_0 \frac{(1-\eta)^2(184 + 258\eta + 222\eta^2 + 76\eta^3 - 75\eta^4)}{184(1+15\eta)}, \quad (28)$$

$$p^2 = 13.6956 \left(\frac{B_0}{s^4 \sigma A_0} \right), \dots \dots \dots \dots \dots \dots \quad (29)$$

and

$$z = \frac{z_1}{19} (6\eta^2 + 28\eta^3 - 15\eta^4), \dots \dots \dots \dots \dots \dots \quad (30)$$

where z_1 is the amplitude at the tip.

APPENDIX III.

The Construction of Cantilever Beams having a known Mode of Torsional Oscillation.

The differential equation of torsional motion is

$$P\ddot{\theta} - \frac{\partial}{\partial y} \left(C \frac{\partial \theta}{\partial y} \right) = 0, \quad \dots \dots \dots \quad (1)$$

where P is the moment of inertia per unit span, and C is the torsional stiffness of unit length. When the beam is oscillating in a single mode

$$\ddot{\theta} = \theta \sin pt, \quad \dots \dots \dots \quad (2)$$

where θ is a function of y only, and equation (1) becomes

$$\frac{d}{dy} \left(C \frac{d\theta}{dy} \right) = -p^2 P \theta. \quad \dots \dots \dots \quad (3)$$

For a cantilever beam of length s the end conditions are

$$\text{For } y = 0, \quad \theta = 0. \quad \dots \dots \dots \quad (4)$$

$$\text{For } y = s, \quad C \frac{d\theta}{dy} = 0. \quad \dots \dots \dots \quad (5)$$

It will be convenient to introduce an auxiliary variable τ' (cp. Appendix II.), which for beams with narrow or fine sections is proportional to (thickness of section) \div (width of section). Thus let

$$C = \frac{NP\tau'^2}{\sigma}, \quad \dots \dots \dots \quad (6)$$

where N is the modulus of rigidity and σ the density. Then equation (3) becomes

$$\frac{d}{dy} \left(P\tau'^2 \frac{d\theta}{dy} \right) = -\frac{\sigma}{N} p^2 P \theta. \quad \dots \dots \dots \quad (7)$$

In order to cover the cases where the beam tapers to zero at the tip, put

$$P = (s-y)^l a(y), \quad \dots \dots \dots \quad (8)$$

$$\tau' = (s-y)^n t(y), \quad \dots \dots \dots \quad (9)$$

and

$$\frac{d\theta}{dy} = (s-y)^q d(y), \quad \dots \dots \dots \quad (10)$$

where $a(s)$, $t(s)$, and $d(s)$ are neither zero nor infinite. Then the left-hand side of (7) contains the factor $(s-y)^{l+2n+q-1}$, and the right-hand side contains $(s-y)^l$, since θ does not vanish at the tip. Hence

$$l+2n+q-1=l, \\ \text{or}$$

$$2n+q=1. \quad \dots \quad \dots \quad \dots \quad \dots \quad (11)$$

Also (5) requires that

$$l+2n+q-1>0,$$

$$\text{or by (11),} \quad l>0. \quad \dots \quad \dots \quad \dots \quad \dots \quad (12)$$

When the shape of the section remains normal near the tip, $n=0$, and if the tip is parabolic in plan form $l=2$. Also by equation (11) $q=1$. Hence for beams of this class

$$P=(s-y)^2a(y). \quad \dots \quad \dots \quad \dots \quad \dots \quad (13)$$

$$\tau'=t(y), \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (14)$$

$$\text{and} \quad \frac{d\theta}{dy}=(s-y)d(y). \quad \dots \quad \dots \quad \dots \quad \dots \quad (15)$$

Example.—Suppose that

$$P=a(s-y)^2, \quad \dots \quad \dots \quad \dots \quad \dots \quad (16)$$

$$\text{and} \quad \frac{d\theta}{dy}=b(s-y)(s+ry). \quad \dots \quad \dots \quad \dots \quad \dots \quad (17)$$

Then by (4) the mode is given by

$$\theta=\frac{b}{6}\{6s^2y+3(r-1)sy^2-2ry^3\}. \quad \dots \quad \dots \quad (18)$$

Therefore (7) becomes

$$\frac{d}{dy}\{(s-y)^3(s+ry)\tau'^2\} \\ =-\left(\frac{p^2\sigma}{6N}\right)(s-y)^2\{6s^2y+3(r-1)sy^2-2ry^3\}. \quad (19)$$

Integrate this equation and choose the constant of integration so that $(s-y)^3$ is a factor of the right-hand side. Then

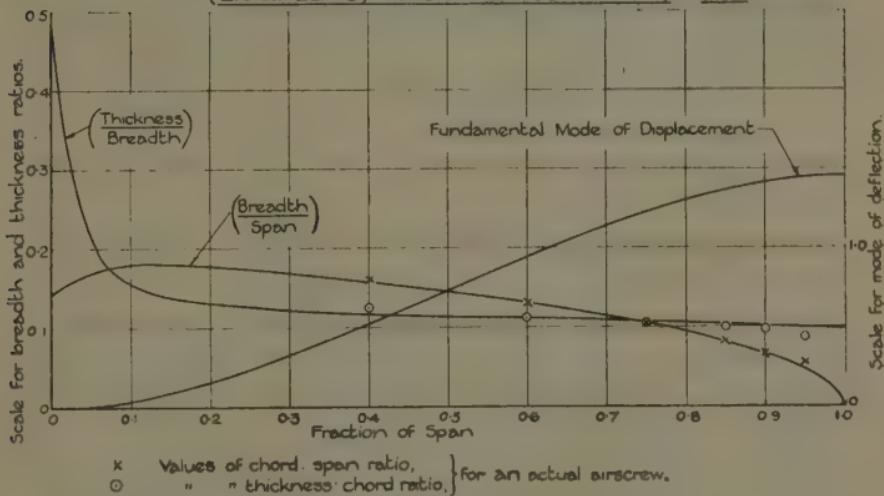
$$\tau'^2=\left(\frac{p^2\sigma}{180N}\right)\frac{(2r+12)s^3+(6r+36)s^2y+(12r-18)sy^2-10ry^3}{(s+ry)} \quad \dots \quad \dots \quad (20)$$

It is found by trial that when $r=120$ the beam whose properties are specified by equations (16) and (20) approximates closely to an airscrew blade. This is clearly shown in fig. 3, where the ratios (width of section) \div (span) and (depth of section) \div (width of section) for a selected blade of the theoretical family are compared with the corresponding ratios for the actual airscrew referred to in Appendix II.

If $\eta = \begin{pmatrix} y \\ s \end{pmatrix}$, then the formulae for the case $r=120$ can

Fig. 3.

CHARACTERISTICS OF A TAPERED BEAM RESEMBLING
AN AIRSCREW BLADE.
(EXAMPLE C; TORSIONAL OSCILLATION). FIG. 3.



be written

$$C = C_0 \frac{(1-\eta)^2(42 + 126\eta + 237\eta^2 - 200\eta^3)}{42(1+120\eta)}, \quad (21)$$

$$P = P_0(1-\eta)^2, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (22)$$

$$p^2 = \frac{5}{7} \left(\frac{C_0}{s^2 P_0} \right), \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (23)$$

and

$$\theta = \left(\frac{\theta_1}{41} \right) (2\eta + 119\eta^2 - 80\eta^3) \dots \quad \dots \quad \dots \quad (24)$$

LXXV. *Statistics of Positrons and Electrons in Equilibrium with Radiation at High Temperatures.* By G. WATAGHIN *.

WE examine the properties of matter and radiation in equilibrium at the temperatures $T \gtrsim 2mc^2/k$ at which the number of photons, with energy $h\nu > 2mc^2$, capable of producing the emission of pairs of electrons from atomic nuclei, cannot be neglected. The creation of pairs modifies the usual statistical laws of Fermi and Dirac for the positrons and electrons, because the number of particles becomes variable with the temperature. Representing the states of positrons and electrons with antisymmetrical wave-functions we can write the usual expression for the probability of a given state of the assemblage of photons, positrons, and electrons :

$$W = \prod_s \frac{(g_s + N_s - 1)!}{(g_s - 1)! N_s!} \cdot \frac{g_s!}{n_s! (g_s - n_s)!} \cdot \frac{g_s!}{n_s'! (g_s - n_s')!} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\}, \quad (1)$$

$$g_s = \frac{8\pi V}{h^3} p^2 dp = \frac{8\pi V}{h^2 c^3} (E_s^2 - m^2 c^4)^{\frac{1}{2}} E_s dE_s,$$

where N_s , n_s , n_s' are the numbers of photons, positrons, and electrons respectively, corresponding to a given interval $p \rightarrow p + dp$ of the momentum and to a given volume V (we put $V = 1$).

In determining the maximum of W , we must take into account the laws of the conservation of energy and electric charge. We suppose that to a first approximation, the interaction between the electrons and positrons is negligible. In this case we can write :

$$\sum_s N_s h\nu_s + \sum_s n_s E_s + \sum_s n_s' E_s' = E = \text{const.}, \quad \dots \quad (2)$$

$$\sum_s n_s' - \sum_s n_s = n = \text{const.} \quad \dots \quad (3)$$

Here we consider the charge and the energy of the nuclei constant. The limiting conditions (2) and (3) are also valid if the density of the nuclei can be neglected.

* Communicated by the Author.

An immediate calculation gives :

$$\left. \begin{aligned} N_s &= \frac{g_s}{e^{kT} - 1}, \\ n_s &= \frac{g_s}{\frac{1}{A} e^{\frac{E_s}{kT}} + 1}, \quad n_s' = \frac{g_s}{\frac{1}{A'} e^{\frac{E_s'}{kT}} + 1}, \end{aligned} \right\} \quad \dots \quad (4)$$

$$A' = \frac{1}{A} \dots \dots \dots \quad (5)$$

The values of A and $A' = A^{-1}$ can be determined as functions of the temperature and the density n_+ of the positrons, or the density n_- of the electrons. In the case $A \ll 1$, putting, for instance, for $E \gg mc^2$ the relativistic approximate expressions

$$p = \frac{E}{c}, \quad g_s = \frac{8\pi}{h^3 c^3} E^2 dE,$$

we find

$$\left. \begin{aligned} n_+ &= \frac{8\pi}{h^3 c^3} \int_0^\infty \frac{E^2 dE}{\frac{1}{A} e^{\frac{E}{kT}} + 1} = \frac{16\pi}{h^3 c^3} (kT)^3 \left[A - \frac{A^2}{2^3} + \frac{A^3}{3^3} - \dots \right], \\ n_- &= \frac{8\pi}{3} \frac{(kT)^3}{h^3 c^3} \cdot (\log A')^3 \left[1 + \frac{\pi^2}{(\log A')^2} - \dots \right]. \end{aligned} \right\} \quad \dots \quad (6)$$

For example, if $kT \sim 10^7 e$ -volt and $A \sim 10^{-34}$, we have $n_+ \sim 1$; $n_- \sim 10^{39}$. If the density of the nuclei at $T=0$ is negligible in respect to the final density $n_-(T)$ of the electrons at the temperature $T \gg 2mc^2$, the creation of pairs by these very high temperatures probably can lead only to the case $n_+ \approx n_-$; $A \approx 1$. Then we obtain

$$n_+ = n_- \sim \frac{16\pi}{h^3 c^3} (kT)^3 \dots \dots \quad (7)$$

Thus the density of positrons and electrons is proportional to T^3 . At the temperature of 10^{11} degrees we have

$$n_+ \sim n_- \sim 10^{34} \dots \dots \quad (7')$$

An essential limitation of the validity of the preceding formula may be due to the existence of an interaction between the electrons and positrons, which in the first non-relativistic approximation is due chiefly to the ordinary coulombian forces. If we take into account this interaction, our problem becomes similar to the problem of the assemblage of neutrons and protons, which appears in the theory of nuclear structure of W. Heisenberg * and E. Majorana †. We can assume the approximate validity of (1) and (3), but we must add in the limiting condition (2) some terms representing the mean potential energy of coulombian forces. This mean potential energy is of the order of magnitude of

$$\frac{n_+^2 e^2}{\sqrt[3]{n_+}} + \frac{n_-^2 e^2}{\sqrt[3]{n_-}} - \frac{n_+ n_- e^2}{\sqrt[3]{n_+ + n_-}}. \quad \dots \quad (8)$$

For the densities of the order of (7') these terms are greater than the total kinetic energy of the assemblage.

If we now calculate the maximum of

$$W - \alpha n - \beta E,$$

where α and β are the usual undetermined multipliers, we obtain the expressions (4), where

$$\left. \begin{aligned} A &\cong e^{-\alpha+\beta\left[\frac{5}{3}n_+^{1/3} - \frac{n_-}{n_+^{1/3}} + \frac{1}{3}\frac{n_+ n_-}{(n_+ + n_-)^{4/3}}\right]e^2}, \\ A' &\cong e^{\alpha+\beta\left[\frac{5}{3}n_-^{1/3} - \frac{n_+}{n_-^{1/3}} + \frac{1}{3}\frac{n_+ n_-}{(n_+ + n_-)^{4/3}}\right]e^2}. \end{aligned} \right\} \quad \dots \quad (9)$$

Obviously the relation (5) is generally no more valid. It is possible to deduce an approximate relation between n_+ , n_- , and α by the method indicated in (6). But the rough calculation with this method gives reasonable results only if we assume that the effects of attractive and repulsive forces balance each other. Therefore we limit ourselves to some remarks, which show that our former results give us the upper limit of the densities n_+ and n_- for the present case. In effect we can assume the creation of pairs takes place only by the collision of a photon with a nucleus. For the inverse process of the transformation of electron pairs into radiation two possibilities

* *Zeits. f. Phys.* lxxvii. p. 1 (1932); lxxviii. p. 156 (1933); lxxx. p. 587 (1933).

† *Zeits. f. Phys.* lxxxii. p. 137 (1933).

are open. A positron may disappear by reacting with an electron and a nucleus; and give rise to a single photon. Or it can disappear by reacting with a free electron and produce two photons.

We want to assume, further, that the interaction is not so large as to forbid the representation of the states of electrons and positrons by the antisymmetrical wave-functions corresponding to the free electrons. For the rough valuation of the statistical laws this assumption seems to us plausible. In this case it is permissible to regard the expression (1) for the probability W as approximately valid.

Then the existence of an interaction between electrons and positrons cannot influence sensibly the former results obtained by the assumption of a negligible interaction. In effect, at a given temperature the number of pairs created by the collision of photons with the nuclei is independent of this interaction, and the inverse process depends from the probability of the collision of three or two bodies (positron, electron, and nucleus). It seems to us plausible to assume that this last probability is not influenced sensibly by the interaction, or can only increase by the effect due to the attractive forces between the electrons and the positrons. In this last case the densities n_+ and n_- would be less, as in the absence of any interaction, and the expressions (6) and (7) would give only the upper limit for these densities.

The processes considered in this paper have probably a certain importance for the temperatures existing inside some stars *. But the state of equilibrium in the stars is complicated by the processes of nuclear disintegration, which we have neglected in the former remarks.

To the processes of creation and destruction of pairs it is possible to apply the laws of Kirchhoff regarding the ratio of the emission and absorption coefficients of the nuclei. In particular the nuclei which emit more pairs must have a greater nuclear absorption coefficient for the incident positrons. This consequence can be verified by the experiments. Also the laws of dissociative equilibrium can be easily established for the processes here considered.

* For instance, they may give origin to the positrons of cosmic radiation. (P. M. S. Blackett, 'Nature,' vol. cxxxii. p. 919, 1933.)

LXXVI. *On the Problem of the Heat Recuperator.* By ARNOLD N. LOWAN, *Columbia University, New York City* *.

ABSTRACT.

By means of the Laplace Transformation, any physical problem characterized by a partial differential equation, the solution of which must satisfy prescribed initial and boundary conditions, can formally be transformed into a boundary problem for an ordinary differential equation.

If the solution of the latter problem can be obtained, the original problem reduces to an integral equation of the first kind, of the type encountered in the "operational" treatment of problems in the Electric Circuit Theory.

The method is particularly powerful when dealing with problems in heat conduction of unusual degree of complexity. A problem of this type is the Thermal History of the Heat Recuperator.

A CIRCULAR cylinder extending from $x=0$ to $x=\infty$, initially at some constant temperature, is heated by means of a hot incompressible fluid flowing in a concentric cylindrical annulus, the outer wall of which is impervious to heat. What is the thermal history of the cylinder and of the fluid?

The above problem is clearly the idealized statement of the problem of the industrial heat recuperator. In actual practice the recuperator is, of course, of finite extent, and is periodically traversed by hot and cold fluid (flue gases and the preheating air respectively). Under these conditions, it is apparent that, after a sufficiently long time, a steady state is reached where the temperature distribution, both in the solid and the fluid, are periodic functions of time.

The problem of the steady state has been investigated by Nusselt ⁽¹⁾, Schmeidler ⁽²⁾, and H. Haussen ⁽³⁾.

A problem closely related to the above is that of the heat transfer in a porous solid (for instance, iron ore) traversed by a hot fluid. This problem has been treated by V. Anzelius ⁽⁴⁾ and T. E. W. Schumann ⁽⁵⁾.

* Communicated by the Author.

All the authors above mentioned assume that the thermal conductivity, both in the fluid and the solid, in the direction parallel to the flow, may be ignored, and that the thermal conductivity in the fluid in the direction normal to the flow is infinite. Anzelius and Schumann further assume that the thermal conductivity in the solid, in the direction normal to the flow, is also infinite. This latter assumption is, however, no longer justified in the case of the problem above stated, and a finite "normal" conductivity for the solid will be assumed.

In view of our assumptions with regard to the thermal conductivity, the thermal history of the finite recuperator, in the first period when it is traversed by the hot fluid, is indistinguishable from that of the infinite recuperator above contemplated. Furthermore, as will be subsequently shown, the temperature distribution in the actual recuperator, which is periodically traversed by hot and cold fluids, may be easily obtained from the temperature distribution in the recuperator above contemplated, for which the initial temperature of the fluid is permanently constant. We, therefore, proceed to obtain the solution of the latter problem.

In the subsequent derivations the following symbols will be used :—

$u(x, r, t)$ =Temperature of the solid cylinder.

$v(x, t)$ =Temperature of the fluid.

R =Radius of the cylinder.

r =Distance from axis of cylinder.

A_2 =Cross-sectional area of the annulus.

K =Thermal conductivity of the solid.

ρ_1 =Density of the solid.

s_1 =Specific heat of the solid.

k =Thermal diffusivity of the solid.

ρ_2 =Density of fluid.

s_2 =Specific heat of fluid.

E =Coefficient of heat transfer between fluid and solid.

v_0 =Initial temperature of fluid at $x=0$.

x =Distance along axis.

t =Time.

a =Linear velocity of the fluid.

$$b = \frac{2\pi RE}{A_2 \rho_2 s_2}; \quad h = \frac{E}{K}; \quad \bar{u} = u(x, R, t).$$

If we assume that the physical constants E , K , a , etc. do not vary with temperature then the mathematical formulation of our problem is as follows :—

$$\frac{\partial u}{\partial t} = k \left(\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} \right) \quad t > 0. \quad \dots \quad (1)$$

$$u = 0 \quad \text{for } t = 0. \quad \dots \quad (2)$$

$$\frac{\partial u}{\partial r} + hu = hv \quad \text{for } r = R. \quad \dots \quad (3)$$

$$\frac{\partial v}{\partial t} + a \frac{\partial v}{\partial x} + bv = bu \quad x \leq at. \quad \dots \quad (4)^*$$

$$v_0 = 0 \quad \text{for } x = 0. \quad \dots \quad (5)$$

It will be convenient to introduce two new independent variables defined as follows :

$$\xi = \frac{b}{a} x; \quad \tau = k \left(t - \frac{x}{a} \right). \quad \dots \quad (6)$$

The system of equations (1) to (5) then becomes

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} \quad \tau > 0. \quad \dots \quad (7)$$

$$\frac{\partial u}{\partial r} + hu = hv \quad \text{for } r = R. \quad \dots \quad (8)$$

$$\frac{\partial v}{\partial \xi} + v = \bar{u} \quad \text{for } \tau > 0. \quad \dots \quad (9)$$

$$u = 0 \quad \text{for } \tau = 0. \quad \dots \quad (10)$$

$$v = v_0 \quad \text{for } \xi = 0. \quad \dots \quad (11)$$

$$v = v_0 e^{-\xi} \quad \text{for } \tau = 0. \quad \dots \quad (12)$$

Equation (9) is an obvious consequence of our assumptions with regard to the thermal conductivities. Indeed $\tau = 0$ represents the frontmost element of the fluid, and

* Riemann-Weber, 'Differentialgleichungen der Physik,' ii. p. 181 (1927).

since no heat is conducted through the solid in the direction parallel to the flow, it follows that all points of a cross-section of the cylinder will still be at the initial temperature 0° when the cross-section has first been reached by the front of the fluid. In particular, $\bar{u}=0$ at $\tau=0$ and (9) yields at once (12).

Let us make the substitution

$$u(r, \xi, \tau) = \alpha r^2 v(\xi, \tau) + w(r, \xi, \tau) \text{ where } \alpha = \frac{h}{R(2+Rh)}. \quad (13)$$

The system (7), (8), and (9) then becomes

$$\frac{\partial w}{\partial \tau} - \left(\frac{\partial^2 w}{\partial r^2} + \frac{1}{r} \frac{\partial w}{\partial r} \right) = 4\alpha v - \alpha r^2 \frac{\partial v}{\partial t} = \phi(r, \xi, \tau), \text{ say,} \quad (14)$$

$$w = -\alpha r^2 v_0 e^{-\xi} = F(r, \xi) \text{ (say) for } \tau=0. \quad (15)$$

$$\frac{\partial w}{\partial r} + hw = 0 \text{ for } r=R. \quad \dots \quad (16)$$

The system of equations (14), (15), (16) formally defines the thermal history of a radioactive cylinder of unit thermal diffusivity, and for which the "radioactivity function" (amount of heat set free per unit volume per unit time) is $\rho_1 s_1 \left(4\alpha v - \alpha r^2 \frac{\partial v}{\partial t} \right)$. The solution of this

problem may be derived by the method developed in a previous paper *, and may be written down at once in the form

$$w(r, \xi, \tau) = \sum_{n=1}^{\infty} e^{-\lambda_n^2 \tau} y_n(r) \int_0^R \rho y_n(\rho) F(\rho) d\rho + \sum_{n=1}^{\infty} e^{-\lambda_n^2 \tau} y_n(r) \left\{ \int_0^R \rho y_n(\rho) d\rho \int_0^{\tau} e^{\lambda_n^2 \eta} \phi(\rho, \xi, \eta) d\eta \right\}, \quad (17)$$

where the summation extends over the characteristic values, and the corresponding normalized characteristic functions of the system

$$\left. \begin{aligned} \frac{\partial^2 y}{\partial r^2} + \frac{1}{r} \frac{\partial y}{\partial r} + \lambda^2 y &= 0 \\ \frac{\partial y}{\partial r} + hy &= 0 \quad \text{for } r=R \end{aligned} \right\} \dots \quad (18)$$

* "On the Cooling of a Radioactive Sphere," by Arnold N. Lowan, Phys. Rev. (Nov. 1, 1933).

It is well known⁽⁶⁾ that

$$y_n(r) = N_n J_0(\lambda_n r), \quad \text{where } N_n^2 = \frac{2}{R^2} \frac{\lambda_n^2}{(h^2 + \lambda_n^2) \{ J_0(\lambda_n R) \}^2} \quad (19-20)$$

and the λ_n 's are the roots of the transcendental equation

$$\lambda J_1(\lambda R) - h J_0(\lambda R) = 0. \quad (21)$$

In view of the significance of the functions ϕ and F from (14) and (15) we ultimately get

$$\begin{aligned} u = & \alpha R^2 v + v_0 e^{-\xi} \sum_{n=1}^{\infty} B_n e^{-\lambda_n^2 \tau} + \sum_{n=1}^{\infty} A_n \int_0^{\tau} e^{\lambda_n^2 (\eta - \tau)} v(\eta) d\eta \\ & + \sum_{n=1}^{\infty} B_n \int_0^{\tau} e^{-\lambda_n^2 (\eta - \tau)} \frac{dv}{d\eta} d\eta, \end{aligned} \quad (22)$$

where

$$\left. \begin{aligned} A_n &= 4\alpha y_n(R) \int_0^R \rho y_n(\rho) d\rho \\ B_n &= -\alpha y_n(R) \int_0^R \rho^3 y_n(\rho) d\rho \end{aligned} \right\} \quad (23)$$

By partial integration of the last integral of (22), and after some obvious transformations (22) becomes

$$\bar{u} = \sum_{n=1}^{\infty} (A_n - \lambda_n^2 B_n) \int_0^{\tau} e^{\lambda_n^2 (\eta - \tau)} v(\eta) d\eta. \quad (22')$$

Substituting (22) in (10) we get

$$\frac{\partial v}{\partial \xi} + v = \int_0^{\tau} v(\xi, \eta) K(\tau - \eta) d\eta, \quad (24)$$

where

$$C_n = A_n - \lambda_n^2 B_n \quad \text{and} \quad K(\eta) = \sum_{n=1}^{\infty} C_n e^{-\lambda_n^2 \eta}. \quad (25)$$

By making use of the easily proven identities

$$\left. \begin{aligned} \int_0^a x J_0(x) dx &= a J_1(a) \\ \int_0^a x^3 J_0(x) dx &= (a^3 - 4a) J_1(a) + 2a^2 J_0(a) \end{aligned} \right\}, \quad (26)$$

we ultimately get

$$C_n = \frac{2h\lambda_n^2}{R(h^2 + \lambda_n^2)}. \quad (27)$$

Our problem has now reduced to that of solving (24), which is a homogeneous partial integro-differential equation. This equation can be solved by a method similar to that employed by B. Van der Pol ⁽¹⁷⁾ in the solution of a linear differential equation, and by S. Koizumi ⁽⁸⁾, for the solution of the Volterra integral equation of the second kind. Let

$$z(\xi, p) = \int_0^\infty e^{-p\eta} v(\xi, \eta) d\eta \quad p > 0. \quad \dots \quad (28)$$

Then, operating on both members of (24) by the Laplace operator, we get

$$\frac{\partial z}{\partial \xi} + z = \int_0^\infty e^{-p\eta} d\eta \int_0^\tau v(\xi, \eta) K(\tau - \eta) d\eta. \quad \dots \quad (29)$$

By making use of "Dirichlet's identity" ⁽⁹⁾,

$$\int_0^t e^{-pt} dt \int_0^x \phi(\xi) K(x - \xi) d\xi = \int_0^t \phi(\xi) d\xi \int_\xi^t e^{-px} K(x - \xi) dx,$$

the last equation becomes

$$\frac{\partial z}{\partial \xi} + z = \int_0^\infty e^{-p\eta} v(\xi, \eta) d\eta \cdot \int_0^\infty e^{-p\eta} K(\eta) d\eta,$$

or

$$\frac{\partial z}{\partial \xi} + \{1 - \phi(p)\} z = 0, \quad \dots \quad (30)$$

where

$$\phi(p) = \sum_{n=1}^{\infty} \frac{C_n}{p + \lambda_n^2} = \frac{2h}{R} \sum_{n=1}^{\infty} \frac{\lambda_n^2}{h^2 + \lambda_n^2} \cdot \frac{1}{p + \lambda_n^2}, \quad \dots \quad (31)$$

Further, the boundary condition (11) under the Laplace transformation, becomes

$$z = \frac{v_0}{p} \quad \text{for } \xi = 0. \quad \dots \quad (32)$$

The solution of (30) and (32) is

$$z(\xi, p) = \frac{v_0}{p} e^{-\xi} \cdot e^{\frac{2h\xi}{R}} \cdot \text{Exp} \sum_{n=1}^{\infty} \frac{\lambda_n^2}{h^2 + \lambda_n^2} \cdot \frac{1}{p + \lambda_n^2} = \frac{1}{p} \psi(\xi, p) \quad (\text{say}) \quad \dots \quad (33)$$

Substituting (33) in (28) we get

$$\begin{aligned} p \int_0^\infty e^{-p\tau} v(\xi, \tau) d\tau &= v_0 e^{-\xi} \cdot e^{\frac{2h\xi}{R}} \cdot \text{Exp} \sum_{n=1}^{\infty} \frac{\lambda_n^2}{h^2 + \lambda_n^2} \cdot \frac{1}{p + \lambda_n^2} \\ &= \psi(p, \xi). \quad (34) \end{aligned}$$

This is an integral equation of the general type encountered in the operational treatment of problems in the Electric Circuit Theory⁽¹⁰⁾. Unfortunately, due to the very complex nature of the function $\psi(\xi, p)$ a solution of (34) cannot be obtained by the direct application of any of the "rules" of the Operational Calculus.

We proceed to indicate a method of solution of (34).

Consider the problem in heat conduction defined by the system

$$\begin{aligned} \frac{\partial T}{\partial t} &= \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r}, \\ T &= F(r) \quad \text{for } t=0, \\ \frac{\partial T}{\partial r} + hT &= 0 \quad \text{for } r=R. \quad \dots \quad (35) \end{aligned}$$

As previously stated, (35) defines the temperature in an infinite cylinder of unit thermal diffusivity, initially at temperature $F(r)$, and radiating into a medium at 0° . The general solution of this problem is *

$$T(r, t) = \frac{2}{R^2} \sum_{n=1}^{\infty} \frac{e^{-\lambda_n^2 t}}{(h^2 + \lambda_n^2) \{J_0(\lambda_n R)\}^2} \int_0^R \rho F(\rho) J_0(\lambda_n \rho) d\rho, \quad (36)$$

where the λ_n 's are the roots of (21).

For $F(r) = 1$, $t = 0$, and $r = R$, (36) becomes, after some obvious transformations,

$$1 \equiv \frac{2}{R^2} \sum_{n=1}^{\infty} \frac{\int_0^{\lambda_n R} x J_0(x) dx}{(h^2 + \lambda_n^2) J_0(\lambda_n R)}. \quad \dots \quad (37)$$

Making use of (26) and (21), the last equation yields the important relation

$$\sum_{n=1}^{\infty} \frac{1}{h^2 + \lambda_n^2} = \frac{R}{2h}. \quad \dots \quad (38)$$

Referring to the definition of $\psi(\xi, p)$ from (34), the latter equation yields

$$\psi(\xi, 0) = v_0 \quad \text{and} \quad \psi(\xi, \infty) = v_0 e^{-\xi}. \quad \dots \quad (39)$$

Accordingly, it is conceivable that we may write

$$\psi(\xi, p) = v_0 e^{-\xi} + \sum_{n=1}^{\infty} \frac{E_n(\xi)}{p + \lambda_n^2}. \quad \dots \quad (40)$$

* *Loc. cit.* vi. p. 118.

The determination of the constant $E_n(\xi)$ will be discussed below.

The integral equation (34) thus becomes

$$p \int_0^\infty e^{-p\tau} v(\xi, \tau) d\tau = v_0 e^{-\xi} + \sum_{n=1}^{\infty} \frac{E_n(\xi)}{p + \lambda_n^2}, \quad \dots \quad (34')$$

the solution of which is readily seen to be

$$v(\xi, \tau) = v_0 e^{-\xi} + \sum_{n=1}^{\infty} \frac{E_n(\xi)}{\lambda_n^2} (1 - e^{-\lambda_n^2 \tau}). \quad \dots \quad (41)$$

From (39) and (40) it follows

$$\sum_{n=1}^{\infty} \frac{E_n(\xi)}{\lambda_n^2} = v_0 - v_0 e^{-\xi}. \quad \dots \quad (42)$$

In view of the last equation (41) may be written in the form

$$v(\xi, \tau) = v_0 - \sum_{n=1}^{\infty} \frac{E_n(\xi)}{\lambda_n^2} e^{-\lambda_n^2 \tau}. \quad \dots \quad (41')$$

It is important to remark that our solution (41) or (41') satisfies the desired boundary conditions (11) and (12). Thus, for $\tau=0$, (41) yields $v=v_0 e^{-\xi}$, in agreement with (12).

For $\xi=0$, it is apparent from (39) and (40) that all the E_n 's vanish, and, therefore, (41) yields $v=v_0$, in agreement with (11). Finally, from (41') we get $v=v_0$ for $\tau=\infty$, a condition which is, of course, obvious from physical considerations.

We now come to the determination of the E_n 's.

Let us assume that we have plotted the function

$$\psi(\xi, p) - v_0 e^{-\xi} = F(\xi, p)$$

versus p for various values of ξ . Since, as will be subsequently shown, the necessary computations are best performed graphically, when referring to the function $F(\xi, p)$, it will be convenient to think of this function in terms of its graphical representation rather than that of its analytical expression.

In accordance with (40), the problem then reduces to that of expanding the function $F(\xi, p)$ in terms of the infinite set of functions

$$U_n(p) = \frac{1}{p + \lambda_n^2}.$$

This is a standard problem in the theory of "Series Expansions of Arbitrary Functions" ⁽¹¹⁾. The method will be briefly indicated, omitting certain questions of rigor.

Let $\phi_n(p)$ be the set of normalized orthogonal functions obtained from the set of the $U_n(p)$'s by the process of orthogonalization.

As is well known, the functions $\phi_n(p)$ are linear combinations of the $U_n(p)$'s. Specifically, we have

$$\begin{aligned}\phi_1(p) &= a_1^1 U_1(p), \\ \phi_2(p) &= a_2^1 U_1(p) + a_2^2 U_2(p), \\ \vdots \\ \phi_n(p) &= a_n^1 U_1(p) + a_n^2 U_2(p) + \dots + a_n^n U_n(p),\end{aligned}\quad . \quad (43)$$

where the coefficients $a_1^1, a_2^1, a_2^2, \dots$, etc. are successively obtained during the process of orthogonalization.

It is now possible to expand the function $F(\xi, p)$ in terms of the normalized orthogonal functions $\phi_n(p)$. Specifically

$$F(\xi, p) = \sum_{n=1}^{\infty} \alpha_n(\xi) \phi_n(p), \quad \text{where } \alpha_n(\xi) = \int_0^{\infty} F(\xi, p) \phi_n(p) dp, \quad . \quad . \quad . \quad (44)$$

In view of (43), the coefficients $E_n(\xi)$ of the expansion

$$F(\xi, p) = \sum_{n=1}^{\infty} \frac{E_n}{p + \lambda_n^2} = \sum_{n=1}^{\infty} E_n U_n(p) \quad . \quad . \quad . \quad (45)$$

assume the form

$$E_1 = \sum_{n=1}^{\infty} \alpha_n a_n'; \quad E_2 = \sum_{n=2}^{\infty} \alpha_n a_n^2; \quad \dots \quad E_i = \sum_{n=i}^{\infty} \alpha_n a_n^i. \quad (46)$$

The computations are necessarily laborious, but, nevertheless, straightforward. For the sake of completeness the systematic method of carrying out the computations will be briefly indicated.

The roots of (21) may be found by plotting the function $\frac{\mu J_1(\mu)}{J_0(\mu)}$ vs. μ and taking the intersection with a parallel

to the axis of the μ 's at a distance $= Rh$; the abscissæ of the points of intersection yield the values of $\mu_n = \lambda_n R$. Having determined the $\phi_n(p)$'s by the process of orthogonalization, the α_n are computed from (44) by graphical integration.

The last step is then the computation of the E_i 's from (46). This may again be done graphically by plotting $\alpha_n a_i^i vs. n$, computing the area under the "broken line" between $n=1$ and $n=\infty$, and subtracting $\frac{1}{2} \alpha_i a_i^i$.

In view of the known convergence of the infinite series in the second member of (40), it follows that $|E_n(\xi)| < \lambda_n^2$. The convergence of the infinite series in (46) is thus implicitly proven.

Our problem is thus completely solved. The temperature of the fluid is given by (41'), where for any particular value of ξ the coefficients $E_n(\xi)$ have been determined by the method just described. The temperature of the cylinder is obtained from (22) and (23), by replacing R by r . In particular, the superficial temperature of the cylinder is given by

$$\bar{u} = \frac{2h}{R} \sum_{n=1}^{\infty} \frac{\lambda_n^2}{h^2 + \lambda_n^2} \int_0^{\tau} e^{-\lambda_n^2(\eta-\tau)} v(\xi, \eta) d\eta \quad \dots \quad (47)$$

(from 22' and 27), where $v(\xi, \eta)$ is to be replaced by its value from (41').

This solution evidently satisfies the boundary condition (9). Further, for $\tau = \infty$ it yields, after some obvious transformations,

$$\bar{u} = \frac{2hv_0}{R} \sum_{n=1}^{\infty} \frac{1}{h^2 + \lambda_n^2} \equiv v_0 \quad (\text{by 38}), \quad \dots \quad (48)$$

which is, of course, obvious from physical considerations.

As was remarked in the beginning of this paper, the preceding treatment is equally applicable to the case of a finite recuperator of length l . It is interesting to compute the total amount of heat Q absorbed by the recuperator during a given interval of time θ . Clearly

$$Q = 2\pi RE \int_0^l \int_0^{\theta} (v - \bar{u}) dx dt.$$

In view of (4) and (6) this equation may be written successively

$$Q = \frac{2\pi RE}{b} \int_0^l \int_0^{\theta} \left(\frac{\partial v}{\partial t} + a \frac{\partial v}{\partial x} \right) dx dt,$$

or

$$Q = -2\pi RE J \int_0^{\xi_1} \int_0^{\tau_1} \frac{\partial v}{\partial \xi} d\xi d\tau, \quad \dots \quad (49)$$

where $J = a/bk$ is the Jacobian of the transformation (6) and ξ_1, τ_1 , are the values of ξ and τ , corresponding to $x=l, t=\theta$. In view of (41) the last equation finally becomes

$$Q = \frac{A_2 \rho_2 s_2 a}{k} \sum_{n=1}^{\infty} \frac{E_n(\xi_1)}{\lambda_n^4} (1 - e^{-\lambda_n^2 \tau_1}). \quad \dots \quad (50)$$

For $\theta = \infty$ we have $\tau_1 = \infty$, and this expression becomes

$$Q = \frac{A_2 \rho_2 s_2 a}{k} \sum_{n=1}^{\infty} \frac{E_n(\xi_1)}{\lambda_n^4}. \quad \dots \quad (51)$$

On the other hand, we evidently have

$$Q = \pi R^2 l p_1 s_1 v_0,$$

and this expression becomes

$$Q = \frac{bR}{2hk} l v_0 A_2 \rho_2 s_2$$

after some obvious transformations. Comparing with (51) we get

$$\sum_{n=1}^{\infty} \frac{E_n(\xi_1)}{\lambda_n^4} = \frac{R v_0 \xi_1}{2h}. \quad \dots \quad (52)$$

This very simple relation must be satisfied by the coefficients $E_n(\xi)$ and should, therefore, serve as a check upon the accuracy of the computed values.

The preceding treatment has yielded the complete solution of the problem of the temperature history of an ideal recuperator, which is permanently traversed by a hot fluid entering the recuperator at temperature v_0 .

As previously pointed out, in actual practice the recuperator is periodically traversed by hot fluid at temperature v_0 and cold fluid at a temperature which may conveniently be taken as 0° .

We now proceed to modify our mathematical analysis so as to take into account the above-mentioned periodicity.

If the period is designated by θ it is clear that the boundary condition (11) must be replaced by

$$v = v_0 \delta(\tau) \quad \text{for } \xi = 0, \quad \dots \quad (11')$$

where

$$\left. \begin{aligned} \delta(\tau) &= 1 \text{ for } 0 < \tau < k\theta; 2k\theta < \tau < 3k\theta; \dots \text{ etc.} \\ \delta(\tau) &= 0 \text{ for } k\theta < \tau < 2k\theta; 3k\theta < \tau < 4k\theta; \dots \text{ etc.} \end{aligned} \right\} (53)$$

Accordingly, equation (32) must be replaced by

$$z = v_0 \int_0^\infty e^{-p\tau} \delta(\tau) d\tau = \frac{v_0}{p} \cdot \frac{1}{1 + e^{-pk\theta}} \quad \text{for } \xi = 0, \quad (32')$$

and (34) by

$$p \int_0^\infty e^{-p\tau} v(\xi, \tau) d\tau = \frac{1}{1 + e^{-pk\theta}} \cdot v_0 e^{-\xi} \cdot e^{\frac{2k\xi}{R}} \cdot \text{Exp} \sum_{n=1}^{\infty} \frac{\lambda_n^2}{h^2 + \lambda_n^2} \cdot \frac{1}{p + \lambda_n^2} \quad (34')$$

or

$$p \int_0^\infty e^{-p\tau} v(\xi, \tau) d\tau = \{1 - e^{-pk\theta} + e^{-2pk\theta} \dots + (-1)^n e^{-npk\theta}\} \psi(\xi, p), \quad (54)$$

where $\psi(\xi, p)$ has the significance shown in (34).

The solution of (54) can easily be obtained. Let V designate our previous solution (41) or (41'). Then

$$p \int_0^\infty e^{-p\tau} V(\xi, \tau) d\tau = \psi(\xi, p). \quad (55)$$

Let further

$$p \int_0^\infty e^{-p\tau} V_n(\xi, \tau) d\tau = e^{-npk\theta} \psi(\xi, p). \quad (56)$$

There is a simple relation between the functions V and V_n . As is well known (7), (12),

$$V_n(\xi, \tau) = \begin{cases} 0 & \text{for } \tau < nk\theta, \\ V(\xi, \tau - dk\theta) & \text{for } \tau > nk\theta. \end{cases} \quad (57)$$

With this significance of the functions $V_n(\xi, \tau)$ the general solution of (54) is

$$v(\xi, \tau) = V(\xi, \tau) - V_1(\xi, \tau) + V_2(\xi, \tau) \dots + (-1)^n V_n(\xi, \tau) \dots \quad (58)$$

It is clear that for $0 < \tau < k\theta$, (58) yields $v(\xi, \tau) \equiv V(\xi, \tau)$ as it should, of course, be. For $k\theta < \tau < 2k\theta$ (58) reduces to the first two terms; for $2k\theta < \tau < 3k\theta$ (58) reduces to the sum of the first three terms, etc.

From (58) it is apparent that having plotted $V(\xi, \tau)$ vs τ for various values of ξ , it is possible to determine by means of the graph thus obtained, the complete thermal history of the recuperator, whether during the "hot stage" or during the "cold stage."

The problem of the temperature history of the actual recuperator is thus completely solved.

It was stated that the determination of the coefficients E_n required in the solution (41) is necessarily laborious. There is, however, one very important case when the computations are enormously simplified. This is the case where the thermal conductivity is very large.

As stated in the beginning of this section, when dealing with the steady state, Haussen has assumed an infinite thermal conductivity in the solid in the direction normal to the flow. The following treatment is applicable not only when the thermal conductivity is actually infinite but when

$$2Rh = 2R \frac{E}{K} \ll 6$$

(E =coefficient of heat transfer, K =thermal conductivity). This assumption is evidently nearer to the true state of affairs than the assumption of an infinite thermal conductivity. It is clearly the more justified the smaller R and the larger the actual conductivity of the solid.

We found, for the temperature $v(\xi, \tau)$ of the fluid, the integral equation

$$p \int_0^\infty e^{-p\tau} v(\xi, \tau) d\tau = v_0 e^{-\xi} \cdot e^{\frac{2h\xi}{R}} \cdot \text{Exp} \sum_{n=1}^{\infty} \frac{\lambda_n^2}{h^2 + \lambda_n^2} \cdot \frac{1}{p + \lambda_n^2},$$

where the λ_n 's are the roots of $\lambda J_1(\lambda R) - h J_0(\lambda R) = 0$.

Let us write

$$\psi(\xi, p) = v_0 e^{-\xi} \cdot e^{2Rh\xi} \cdot \text{Exp} \sum_{n=1}^{\infty} \frac{\mu_n^2}{R^2 h^2 + \mu_n^2} \cdot \frac{1}{R^2 p + \mu_n^2},$$

where now the μ_n 's are the roots of $\mu J_1(\mu) - Rh J_0(\mu) = 0$.

We found

$$\sum_{n=1}^{\infty} \frac{1}{h^2 + \lambda_n^2} = \frac{R}{2h},$$

therefore

$$\sum_{n=1}^{\infty} \frac{1}{R^2 h^2 + \mu_n^2} = \frac{1}{2Rh}.$$

Let

$$\varphi(p) = \sum_{n=1}^{\infty} \frac{\mu_n^2}{R^2 h^2 + \mu_n^2} \cdot \frac{1}{R^2 p + \mu_n^2},$$

then

$$\varphi(0) = \sum_{n=1}^{\infty} \frac{1}{R^2 h^2 + \mu_n^2} = \frac{1}{R^2 h^2 + \mu_1^2} + \sum_{n=2}^{\infty} \frac{1}{R^2 h^2 + \mu_n^2}.$$

Let us estimate the second term of the last equation. We evidently have

$$\sum_{n=2}^{\infty} \frac{1}{R^2 h^2 + \mu_n^2} < \sum_{n=1}^{\infty} \frac{1}{x_n^2},$$

where the x_n 's are the roots of $J_1(x)=0$. But we have ⁽¹³⁾

$$x_n > n\pi \quad \text{or} \quad \frac{1}{x_n^2} < \frac{1}{n^2 \pi^2},$$

whence

$$\sum_{n=2}^{\infty} \frac{1}{R^2 h^2 + \mu_n^2} < \frac{1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{1}{\pi^2} \cdot \frac{\pi^2}{6} = \frac{1}{6}.$$

If we assume that $2Rh \ll 6$, then it is clear that $\varphi(0)$ and, therefore, also $\varphi(p)$ reduce to the first term of the expansion.

From

$$\frac{1}{2Rh} \sim \frac{1}{R^2 h^2 + \mu_1^2} \quad \text{we get} \quad \mu_1^2 = \sim 2Rh,$$

and, therefore,

$$\psi(\xi, p) = v_0 e^{-\xi} \cdot e^{\frac{2Rh\xi}{R^2 p + 2Rh}}.$$

The problem has thus reduced to solving the integral equation

$$p \int_0^{\infty} e^{-p\tau} v(\xi, \tau) d\tau = v_0 e^{-\xi} \cdot e^{\frac{2Rh\xi}{R^2 p + 2Rh}} = v_0 e^{-\xi} \cdot e^{-\frac{2Rh\xi}{R^2 (p + \frac{2}{R})}}. \quad (59)$$

Let

$$p \int_0^{\infty} e^{-p\tau} h(\xi, \tau) d\tau = v_0 e^{-\xi} \cdot e^{\frac{2Rh\xi}{R^2 p}}. \quad . . . \quad (60)$$

Then it is known [†]

$$v(\xi, \tau) = e^{-2\frac{h}{R}\tau} h(\xi, \tau) + \frac{2h}{R} \int_0^{\tau} e^{-2\frac{h}{R}t} h(\xi, t) dt. \quad . \quad (61)$$

* For identity, $\sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}$, see Riemann-Weber, i. p. 161.

† J. Carson, *loc. cit.* x. p. 45.

To get the solution of (60) we write the second member in the form

$$v_0 e^{-\xi} \left\{ 1 + \frac{2 \frac{h \xi}{R}}{1!} \cdot \frac{1}{p} + \frac{\left(2 \frac{h \xi}{R}\right)^2}{2!} \frac{1}{p^2} + \dots \right\}.$$

Replacing p^{-n} by $\frac{\tau^n}{n!}$, the desired solution is

$$h(\xi, \tau) = v_0 e^{-\xi} \left\{ 1 + \frac{2h \xi \tau}{R} + \frac{\left(2 \frac{h}{R} \xi \tau\right)^2}{(1!)^2} + \dots + \frac{\left(2 \frac{h}{R} \xi \tau\right)^n}{(n!)^2} + \dots \right\}$$

or

$$h(\xi, \tau) = v_0 e^{-\xi} J_0 \left(2i \sqrt{2 \frac{h}{R} \xi \tau} \right) = v_0 e^{-\xi} I_0 \left(2 \sqrt{2 \frac{h}{R} \xi \tau} \right). \quad \dots \quad (62)$$

(The values of $I_0(x)$ are tabulated in A. Gray & G. B. Matthews, 'A Treatise on Bessel Functions' (1922).)

The complete solution of our problem now assumes the elegant form

$$v(\xi, \tau) = v_0 e^{-\xi} \left\{ e^{-2 \frac{h}{R} \tau} I_0 \left(2 \sqrt{2 \frac{h}{R} \xi \tau} \right) + 2 \frac{h}{R} \int_0^\tau e^{-2 \frac{h}{R} t} I_0 \left(2 \sqrt{2 \frac{h}{R} \xi t} \right) dt \right\}. \quad (63)$$

(It is readily seen that ξ is dimensionless and that the dimensions of h and τ are L^{-1} and L^2 respectively. Thus (63) is dimensionally correct.)

It can be shown that this solution satisfies our boundary conditions. Indeed, for $\tau=0$ we have $v=v_0 e^{-\xi}$ in agreement with (12). For $\xi=0$, the last integral becomes

$$\frac{1}{2} \frac{h}{R} \left\{ 1 - e^{-2 \frac{h}{R} \tau} \right\}.$$

and, therefore, $v=v_0$ in agreement with (11).

Finally, it can be shown that $v \rightarrow v_0$ for $\tau \rightarrow \infty$. Indeed, since ⁽¹⁴⁾

$$J_0(ix) \rightarrow \frac{e^x}{\sqrt{2\pi x}} \quad \text{for } x \rightarrow \infty,$$

it is readily shown that the first term in the brackets in (63) $\rightarrow 0$ as $\tau \rightarrow \infty$.

Further, let u designate the second term in the brackets. Then, if we put

$$t = \eta^2; \quad a^2 = 2 \frac{h}{R}; \quad b^2 = -8 \frac{h}{R} \xi,$$

we get

$$u = 2a^2 \int_0^\infty e^{-a^2 \eta^2} \cdot \eta J_0(b\eta) d\eta.$$

The value of the latter integral is ⁽¹⁵⁾ $\frac{1}{2a^2} \cdot e^{-\frac{b^2}{4a^2}}$.

Substituting for a and b , we get $u = e^\xi$, and, therefore, $\lim_{\tau \rightarrow \infty} v = v_0$, as it should be.

After an obvious transformation, our solution (63) may be rewritten in the more convenient form

$$v(\xi, \tau) = v_0 e^{-\xi} \left\{ e^{-2 \frac{h}{R} \tau} I_0 \left(2 \sqrt{2 \frac{h}{R} \tau \xi} \right) + \int_0^{2 \frac{h}{R} \tau} e^{-\eta} I_0(2\sqrt{\xi\eta}) d\eta \right\}. \quad (64)$$

The computations, on the basis of this formula, are, of course, enormously simpler than those described in the previous theory. In fact, the first term in brackets can be readily calculated, since the values of $I_0(x)$ are tabulated. Furthermore, if we plot

$$S(x) = \int_0^x e^{-\eta} I_0(2\sqrt{\xi\eta}) d\eta, \dots \quad (65)$$

vs. x for various values of ξ , the set of curves thus obtained are of universal applicability, and may be used for computing the temperature history in any "specific" recuperator corresponding to specific numerical values of the physical parameters R, a, E , etc.

Before proceeding to illustrate the above theory to a specific numerical example, let us investigate the modification introduced in the formula for the temperature of the cylinder by our assumption $2Rh \ll 6$.

We found for the superficial temperature of the cylinder

$$\bar{u} = \frac{2h}{R} \sum_{n=1}^{\infty} \frac{\lambda_n^2 e^{-\lambda_n^2 \tau}}{h^2 + \lambda_n^2} \int_0^{\tau} e^{\lambda_n^2 \eta} v(\xi, \eta) d\eta.$$

In view of our assumption regarding the thermal conductivity, the above formula represents the temperature of the cylinder at practically all points of a cross-section and the "bar" is no longer necessary. We may write

$$\begin{aligned}
 u &= \frac{2h}{R} \sum_{n=1}^{\infty} e^{-\lambda_n^2 \tau} \int_0^{\tau} e^{\lambda_n^2 \eta} v(\xi, \eta) d\eta \\
 &= \frac{2h}{R} e^{-\lambda_1^2 \tau} \int_0^{\tau} e^{\lambda_1^2 \eta} v(\xi, \eta) d\eta \\
 &+ \frac{2h}{R} \sum_{n=2}^{\infty} e^{-\lambda_n^2 \tau} \int_0^{\tau} e^{\lambda_n^2 \eta} v(\xi, \eta) d\eta = U_1 + U_2 \quad (\text{say}) \\
 &\quad \dots \quad (66)
 \end{aligned}$$

Let us estimate U_2 . We have evidently

$$U_2 < \frac{2h}{R} v(\xi, \tau) \sum_{n=2}^{\infty} e^{-\lambda_n^2 \tau} \int_0^{\tau} e^{\lambda_n^2 \eta} d\eta$$

or

$$U_2 < \frac{2h}{R} v(\xi, \tau) \sum_{n=2}^{\infty} \frac{1 - e^{-\lambda_n^2 \tau}}{\lambda_n^2}. \quad \dots \quad (67)$$

It is clear that $U_2 \rightarrow 0$ when $h \rightarrow 0$.

In a similar manner we have

$$U_1 < \frac{2h}{R} v(\xi, \tau) \left\{ \frac{1 - e^{-\lambda_1^2 \tau}}{\lambda_1^2} \right\}.$$

But we have previously found

$$\lambda_1^2 = \frac{1}{R^2} \mu_1^2 \sim \frac{1}{R^2} \cdot 2Rh = 2 \frac{h}{R},$$

whence $U_1 < (1 - e^{-\lambda_1^2 \tau}) v(\xi, \tau) = U$ (say), \dots (68)

or since

$$\tau = \frac{K}{\rho_1 s_1} \left(t - \frac{x}{a} \right)$$

it follows

$$u \sim U_1 < \left\{ 1 - e^{-\frac{2E}{R\rho_1 s_1} \left(t - \frac{x}{a} \right)} \right\} v(\xi, \tau). \quad \dots \quad (69)$$

The actual evaluation of U_1 can be carried out by graphical integration once $v(\xi, \tau)$ has been computed. If in (69), $v(\xi, \tau)$ is replaced by $v_0 e^{-\xi}$, we evidently obtain a lower limit for u .

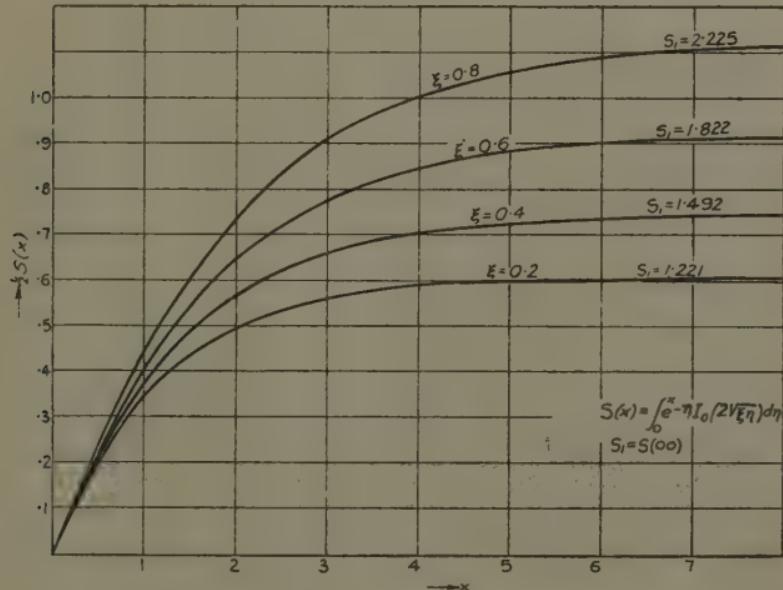
Numerical Illustration.

As previously mentioned, the computations for any specific case can be carried out by means of a table of values for the "S" integrals defined by (65).

The following is a partial table of values for the "S" integrals:—

ξ	x	0.	1.	2.	3.	4.	5.	6.	∞ .
0.2	0	0.685	0.988	1.122	1.182	1.207	1.217	1.221	
0.4	0	0.744	1.129	1.321	1.413	1.457	1.478	1.492	
0.6	0	0.805	1.283	1.550	1.689	1.764	1.804	1.882	
0.8	0	0.874	1.460	1.814	2.014	2.123	2.183	2.225	

The "S" integral curves are shown in the accompanying graph.



To illustrate the use of these curves, consider the specific examples of a thermal recuperator defined by the following values of the physical parameters:—

$$R = 0.25 \text{ m.}; \quad a = 0.5 \frac{\text{m.}}{\text{sec.}} = 1800 \frac{\text{m.}}{\text{hour}};$$

$$E = 12 \frac{\text{K cal.}}{\text{m.}^2 \times \text{hr.} \times {}^\circ\text{C.}}; \quad \rho_2 s_2 = 0.286 \frac{\text{K cal.}}{\text{m.}^3 \times {}^\circ\text{C.}}$$

t (hours)	0	0.50	1.0	1.5	2.0	2.5	3.0	3.50	4.0
$\frac{h}{2R}\tau$	0	0.68	1.365	1.94	2.76	3.41	4.095	4.77	5.53
$M = e^{-2\frac{h}{R}\tau}$	1	0.50	0.255	0.143	0.063	0.033	0.016	0.008	0.004
$\frac{h}{2R}\xi\tau$	0	0.27	0.547	0.82	1.095	1.37	1.641	1.92	2.18
$2\sqrt{\frac{h}{2R}\xi\tau}$	0	1.04	1.478	1.81	2.09	2.34	2.56	2.46	2.95
$N = I_0\left(2\sqrt{\frac{h}{2R}\xi\tau}\right)$	1	1.29	1.62	1.99	2.43	2.91	3.44	3.19	4.68
MN	1	0.64	0.415	0.28	0.153	0.096	0.055	0.025	0.019
$S\left(\frac{2h}{R}\tau\right)$	0	0.55	0.92	1.10	1.28	1.36	1.42	1.44	1.46
$P = MN + S\left(\frac{2h}{R}\tau\right)$. .	1.0	1.19	1.33	1.38	1.43	1.45	1.46	1.47	1.48
$\frac{v}{v_0} = e^{-\xi\tau}P$	0.67	0.80	0.90	0.92	0.96	0.97	0.98	—	0.99
$1 - e^{-2\frac{h}{R}\tau}$	0	0.5	0.745	0.857	0.937	0.967	0.983	0.992	0.996
U/v_0	0	0.415	0.67	0.80	0.90	0.94	0.96	—	0.99

$$\rho_1 s_1 = 70 \frac{\text{K cal.}}{\text{m.}^3 \times {}^\circ\text{C.}} \quad (\text{corresponding to}$$

$$\rho_1 = 2.8 \frac{\text{gm.}}{\text{cm.}^3}, \quad s_1 = 0.25 \frac{\text{cal.}}{\text{gm.} \times {}^\circ\text{C.}});$$

$$A_2 = 1 \text{ m.}^2.$$

What is the temperature of the fluid and that of the cylinder at a distance $x = 11 \text{ m.}$?

Referring to the definitions of our symbols we get

$$b = \frac{2\pi RE}{A_2 \rho_2 s_2} = \frac{2\pi \times 0.25 \times 12}{1 \times 0.286} = 66 \text{ reciprocal hours};$$

$$\xi = \frac{b}{a} x = \frac{66 \times 11}{1800} = 0.4 \text{ (dimensionless);}$$

$$2 \frac{h}{R} \tau = \frac{2E}{KR} \cdot \frac{K}{\rho_1 s_1} \left(t - \frac{x}{a} \right) \sim 1.365 t; \quad 2 \frac{h}{R} \xi \tau \sim 0.547 t.$$

The systematic computation of the temperature $v(x, t)$ of the fluid for $x = 11 \text{ m.}$ is shown in the accompanying table. With regard to the temperature of the solid, it may be briefly stated that it is very close to the upper limit U above considered, as may be readily ascertained by calculating U_1 from (66) by graphical integration.

Bibliography.

- (1) W. Nusselt, *Zeitschr. d. Ver. d. deut. Ing.* (1924).
- (2) W. Schmeidler, *Zeitschr. Angew. Math. & Mech.* viii. p. 385 (1928).
- (3) H. Haussen, *Zeitschr. Angew. Math. & Mech.* ix. p. 173 (1929).
- (4) V. Anzelius, *Zeitschr. Angew. Math. & Mech.* vi. p. 291 (1926).
- (5) T. E. W. Schumann, *Journ. Franklin Institute*, ccviii. p. 405 (1929).
- (6) H. Carslaw, *Introd. Math. Theory of Conduction of Heat in Solids* (1921).
- (7) B. Van der Pol, *Phil. Mag. ser. 7*, viii. p. 861 (1929).
- (8) S. Koizumi, *Phil. Mag. ser. 7*, xi. p. 432 (1931).
- (9) V. Volterra, 'Lecons sur les Equations Intégrales et Intégro-Différentielles,' p. 36 (1913).
- (10) J. R. Carson, 'Operational Calculus and the Electric Circuit Theory' (1926).
- (11) R. Courant & D. Hilbert, *Methoden der Math. Phys.* vol. i. chap. ii. (1924).
- (12) H. Jeffreys, *Operational Calculus* : Cambridge Tracts of Math. & Math. Phys. no. 23.
- (13) Gray & Matthews, 'Treatise on Bessel Functions,' chap. vii. (1922).
- (14) Jahnke & Emde, 'Funktionentafeln,' p. 109 (1909).
- (15) G. N. Watson, 'Theory of Bessel Functions,' p. 394 (1922).

LXXVII. *The Magnetic Rotatory Dispersion and the Refraction of Aqueous Solutions of Cerous Sulphate.* By R. W. ROBERTS, *D.Sc.*, L. A. WALLACE, *M.Sc.*, and I. T. PIERCE, *M.Sc.*, *The University, Liverpool* *.

I. INTRODUCTION.

AS a result of low temperature investigations on the magnetic rotatory dispersion of the crystal tysonite, Becquerel and de Haas † found, by using Ladenburg's formula ‡, that the large negative rotation of tysonite was due to the presence of an intense absorption band with wave-length 2370 Å. Although tysonite is a complex fluoride of the ions La^{+++} , Ce^{+++} , Pr^{+++} , and Nd^{+++} , they attributed this band to the ion Ce^{+++} . The calculated wave-length of this absorption band is in fair agreement with the observations of Gibbs and White §, who found that there were lines in the emission spectrum of Ce IV with wave-lengths 2779 and 2458 Å. However, the ground state suggested by Gibbs and White from emission data is at variance with the ground state of Ce^{+++} predicted from Hund's theory ||. Furthermore, the value of 1 Bohr magneton for the magnetic moment of the cerous ion as deduced by Becquerel and de Haas ¶ from tysonite is in strong disagreement with the value 2.54 Bohr magnetons obtained from susceptibility measurements. In view of these facts it appeared to us that further work on the cerous ion under different conditions would be of interest.

Although in many ways it is desirable to work at low temperatures when studying paramagnetic rotation phenomena, the present investigation has been carried out at 22.2° C., at which temperature we could use ordinary polarimetric methods. By so doing we have been able to extend our observations to wave-length 3128 Å., to obtain all the necessary data for the comparison between theory and experiment, and, of course, to avoid

* Communicated by Prof. L. R. Wilberforce, M.A.

† J. Becquerel and W. J. de Haas, *Zeits. f. Phys.* lvii. p. 11 (1929).

‡ R. Ladenburg, *Zeits. f. Phys.* xxx. p. 898 (1925).

§ R. C. Gibbs and H. E. White, *Phys. Rev.* xxxiii. p. 157 (1929).

|| F. Hund, *Zeits. f. Phys.* xxxiii. p. 855 (1925).

¶ J. Becquerel and W. J. de Haas, *Zeits. f. Phys.* lii. p. 678 (1928).

the cryomagnetic anomalies which complicate low temperature work.

By the employment of solutions instead of crystals containing the cerous ion, the experimental difficulties due to double refraction and the theoretical difficulties arising from the presence of inter-atomic fields in crystals are avoided.

While we were engaged on this work Bose and Datta * and Freed † have published data concerning the absorption of the cerous ion in solution and in crystals respectively. A statement of the results of our preliminary work, together with some absorption data, has already been published ‡. We have since extended our observations to solutions of greater concentration than those used in the preliminary work and have confirmed these results §. In this paper we shall deal only with the data referring to these stronger solutions. In spite of the smaller solubility of cerous sulphate compared with other cerous salts, we have chosen cerous sulphate solutions for the purpose of investigation, as the magnetic rotatory dispersion due to the SO_4^{2-} ion is small compared with that due to most ions.

We have made magnetic rotation and refraction measurements on three solutions of cerous sulphate, hereinafter denoted by A, B, and C, one solution of lanthanous sulphate hereinafter denoted by D, and water. The lanthanous sulphate solution was investigated in order to obtain an estimate of the rotation due to the sulphate ion and the core of the cerous ion, which for this purpose we have assumed to be the same as that of the lanthanous ion.

II. THE SOLUTIONS.

The cerium solutions were prepared from purified cerous sulphate, which was stated to be free from ceric sulphate, but to contain a trace of praseodymium, and slighter traces of neodymium and lanthanum. The lanthanum solution was prepared from purified lanthanous sulphate.

Table I. gives the concentration in grams, W, of anhydrous cerous (or lanthanous) sulphate per 100 grams of

* D. M. Bose and S. Datta, 'Nature,' cxxviii. p. 270 (1931).

† S. Freed, Phys. Rev. xxxviii. p. 2122 (1931).

‡ R. W. Roberts and L. A. Wallace, 'Nature,' cxxx. p. 890 (1932).

§ *Ibid.* cxxxii. p. 782 (1933).

solution, and the densities of the solutions for the temperatures $18\cdot0^{\circ}\text{ C.}$ and $22\cdot2^{\circ}\text{ C.}$ at which the refractivity and magnetic rotation measurements respectively were made. The error in the density estimated from the weighings is $\pm 0\cdot00001$.

The concentrations were determined by evaporating a known weight of each solution, contained in a Pyrex weighing bottle and then dehydrating the crystals so formed by prolonged heating in an electric furnace, maintained at 450° C. for the cerous solutions and at

TABLE I.

W = weight of anhydrous cerous (or lanthanous) sulphate in 100 gm. of solution.

$d_4^{18\cdot0}$, $d_4^{22\cdot2}$ = densities of solution at $18\cdot0^{\circ}\text{ C.}$ and $22\cdot2^{\circ}\text{ C.}$ respectively.

Solution.	$W.$	$d_4^{18\cdot0}.$	$d_4^{22\cdot2}.$
A (Ce)	10.3562	1.10803	1.10656
B (Ce)	7.2422	1.07326	1.07195
C (Ce)	4.3780	1.04287	1.04168
D (La)	2.6635	1.02602	1.02499

600° C. for the lanthanous solution. The heating was repeated until the weight remained constant to within $0\cdot1$ mgm. The error in the concentration is $\pm 0\cdot0004$.

For the temperature range $18\cdot0^{\circ}\text{ C.}-22\cdot2^{\circ}\text{ C.}$ solution A was supersaturated, while B was almost saturated. It was not found possible to use solutions having a greater concentration than that of A.

III. MAGNETIC ROTATION MEASUREMENTS.

PART I.—*Measurements in the Violet and near Ultra-violet.*

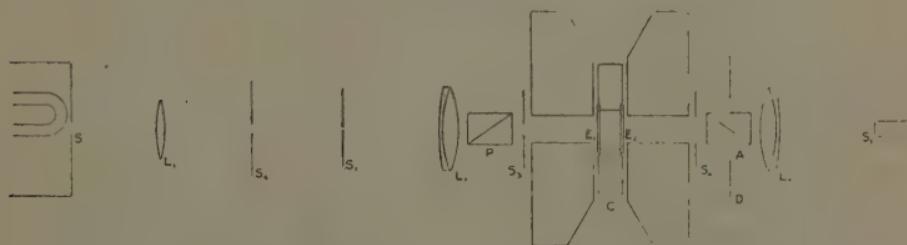
We have used the method of Bruhat and Pauthenier * to obtain the magnetic rotation of our solutions for the wave-lengths 4350 †, 4047 , 3652 , 3341 , and 3128 \AA.

* Rev. d'Opt. vi. p. 163 (1927).

† A centre of gravity wave-length derived from the Hg lines 4358 , 4347 , and 4339 \AA.

Fig. 1 shows the essential parts of the apparatus. Light from one of the limbs of a quartz mercury vapour lamp was limited by a stop S_1 , and focussed by means of the quartz lens L_1 on the stop S_2 at the focus of a quartz fluorite achromate L_2 of 32 cm. focal length. After passing through the glycerine-cemented polarizer P , the beam was limited by the stop S_3 , and then passed without further limitation through the prismatic cell C supported between the pole pieces of a large Du Bois electromagnet, the stop S_4 , the glycerine-cemented analyser A , and the quartz fluorite lens L_3 of 32 cm. focal length. At the focus of this lens was placed the slit S_2^1 of a small quartz spectrograph. An image of S_2 was thus formed on S_2^1 . In addition to the above-mentioned stops, a further

Fig. 1.



Diameters of stops: $S_4^1 = 4.14$ mm.; $S_2 = 1.24$ mm.;
 $S_3 = 6.27$ mm.

stop S_4^1 , the conjugate of S_4 with respect to L_2 , was used to diminish scattered light.

Owing to the lack of uniformity of the magnetic field between the pole pieces of the electromagnet, it was necessary, in order to obtain trustworthy results, to define the geometrical path of the beam with precision. For this purpose all lenses were provided with means for centering, and all stops, with the exception of S_4 , could be displaced through small distances perpendicular to the axis of the beam. S_4 was permanently centred on the common axis of rotation of the divided circle D , the nicol A , and the lens L_3 , which were mounted in a tube rigidly fixed to one of the borings of the electromagnet.

The axis of the apparatus was defined as the axis of rotation of the divided circle when the electromagnet

was excited. To adjust the apparatus, the following operations were carried out in the order given :—

- (1) L_3 was centred on the axis of rotation.
- (2) A stop, 1 mm. in diameter, was introduced at S_2^1 and was centred on the axis by autocollimation effected on the end faces of A. These end faces were then set perpendicular to the axis.
- (3) End plate E_1 of the cell (empty and dry) was set perpendicular to the axis.
- (4) S_3 , placed so that $S_3E_1=E_1S_4$ *, was centred on the axis.
- (5) S_1 was centred on the axis.
- (6) L_2 was centred on the axis.
- (7) The stop S_4^1 was set to coincide with the image of S_4 formed by L_2 .
- (8) S_2 was set to coincide with the image of S_2^1 formed by L_3 and L_2 .
- (9) L_1 was centred on the axis.
- (10) The axis of the polarizer was set at a small but definite angle to the axis of the apparatus. This was necessary in order to prevent light successively reflected from the end plate E_2 and the polarizer end faces from entering the slit of the spectrograph.
- (11) For the purpose of control during the course of the observations the cell was readjusted so that face E_2 was perpendicular to the axis.

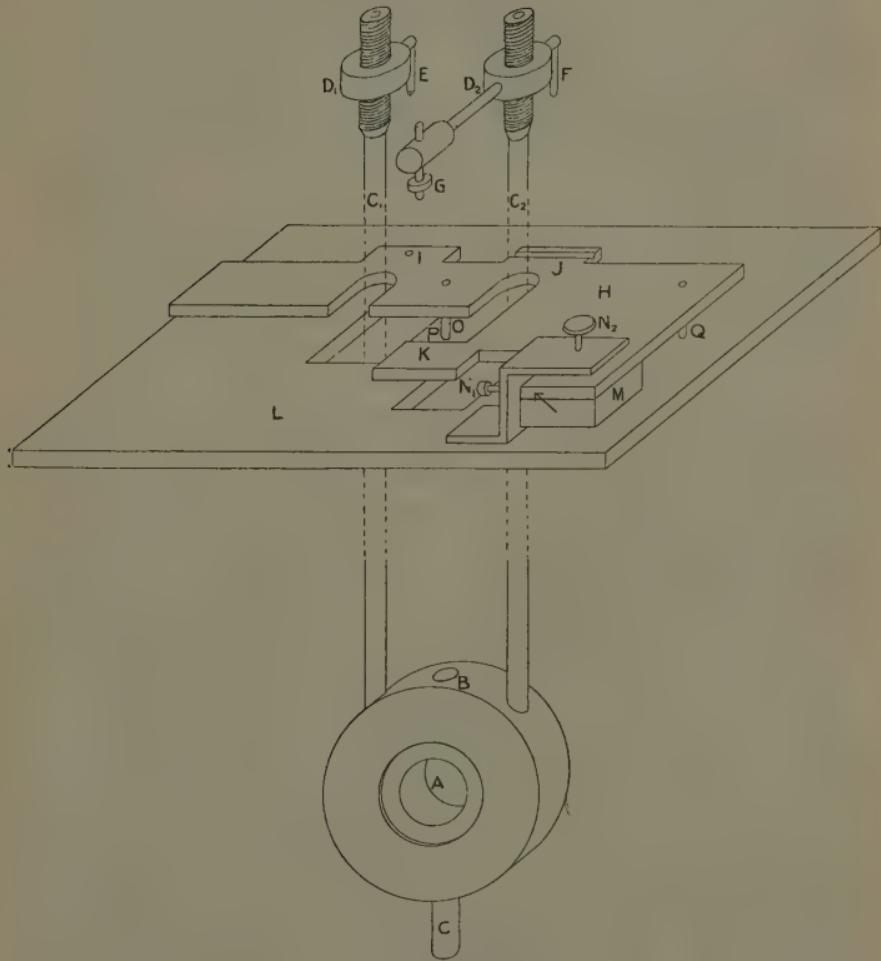
All these adjustments were made while the current was flowing through the electromagnet in either sense, as, in addition to the alteration of the axis of rotation of the apparatus on the application of the field, there was a slight yield of the support carrying the cell. Owing to the smallness of this yield, however, the cell always took up the same position every time the current was made.

Fig. 2 shows the method adopted for the construction and mounting of the brass cell which contained the

* For this adjustment see *Handbuch der Physik*, xix. s. 734 (article by O. Schönrock).

solution under test in the boring A closed by end plates. A second boring, B, served to admit the solution into the cell and to hold a stopper, through which projected a thermojunction enclosed in a thin glass sheath. The

Fig. 2.



The cell mount.

second thermojunction was kept in melting ice in a Dewar vessel.

A moving coil galvanometer recorded the temperature of the solution, which was maintained at 22.2°C . to within $\pm 1^{\circ}\text{C}$. by means of a stream of water forced through the brass tubes C, C₁, C₂ by a circulator immersed in a

reservoir. The temperature of this reservoir was under the immediate control of the observer watching the galvanometer.

The borings A and B, as well as the flats for the end plates, were gold plated to prevent chemical action. As, however, this was found insufficient, a further protection was secured by means of a thin film of paraffin-wax.

The cell was mounted so that when required it could easily be removed from the apparatus and reset in exactly the same position. The tubes C₁, C₂, threaded on the outside, carried nuts D₁ and D₂. To D₁ was attached an arm with a trihedral contact leg E, while D₂ carried the two legs F and G with hemispherical ends. These legs contacted with the brass plate H at the hole I, the slot J, and the plane K. The cell was thus suspended from H by means of the cooling-tubes C₁ and C₂.

The plate H in turn was maintained, by means of a six-point contact, against the support L, which was pinned to both limbs of the electromagnet. The method of choosing the six-point contacts to give the necessary adjustments to the cell has been taken from the elegant design of the mounting of the parallel plate in the Hilger Students' Interferometer *, and so a brief description will suffice. A block M was attached to H in the position shown. This was held against the rounded ends of two screws N₁ and N₂ by means of a spring indicated on the figure by an arrow. To the plate H also was attached a trihedral leg O, and a leg Q with a rounded end. O rested in a circular hole, P, drilled into the plate L vertically above the centre of the polar air gap, while Q rested on the plane part of L. The cell could thus be rotated about a vertical axis through the centre of P by a movement of N₁, and about the horizontal axis PQ by a movement of N₂. The initial adjustments of the cell between the pole pieces was facilitated by making the leg G of adjustable length. When the correct length of G was found, it was locked in position.

PART 2.—*Measurements in the Visible Spectrum.*

We have made observations on the mercury lines 5780 Å. and 5461 Å. for the solutions A, B, C, D, and for water.

* A. F. C. Pollard, *Journ. Scient. Instr.* iv. p. 184 (1927).

These wave-lengths were selected from the radiation of a quartz mercury vapour lamp by means of a van Cittert double monochromator with glass components which was constructed in the laboratory. The exit stop, 0.9 mm. in diameter, of this instrument formed the entrance stop of the polarimeter which was formed by replacing the lens L_2 (fig. 1) by a plano-convex lens L_2^1 of 20 cm. focal length, the polarizer P by a two-part Lippich polarizer, and the lens L_3 by a small astronomical telescope. The effective stops in this arrangement were thus the image of the entrance stop of the polarimeter formed by means of the lens L_2^1 in the plane of the stop S_4 , and S_3 .

It will be seen that the opening of the beam used in the photographic method, already described, differs from that used in the visual observations. Owing to the non-homogeneity of the magnetic field, the two methods will give different rotations for the same wave-length. To correlate the visual and photographic results, we have determined the magnetic rotation of water for wavelength 4350 Å., using the same beams as in the visual and photographic methods. This was carried out in both cases by photography, owing to the insensitiveness of the eye in the violet. An attempt to photograph the half shadow settings did not give the necessary precision, so that, for the purpose of determining the correlation factor, we actually replaced the Lippich by the polarizer P of the arrangement described in Part 1.

In addition to the observations on the Hg lines 5780 Å. and 5461 Å., we have determined the magnetic rotation of water for the Na line 5893 Å., for the purpose of reducing our observed rotations to Verdet constants. The sodium line was produced by burning soda glass in an iron arc and filtering the light through the double monochromator.

The method of adjusting the apparatus for the visual measurements followed almost the same steps as previously described.

IV. THE OBSERVATIONS.

During the taking of all the plates and the visual observations, the current through the electromagnet was kept adjusted to the value of 16 amperes by means of a carbon pressure resistance. The internal windings

and pole pieces of the electromagnet were water cooled. On the grounds of economy and convenience, it was not possible to run the current sufficiently long for a thermal steady state to be reached.

Each rotation has been obtained from two plates corresponding to the two senses of the current through the coils of the electromagnet. On each plate were recorded the images referring to ten or twelve settings of the analyser in the neighbourhood of the extinction position. The exposure times in minutes adopted for the different wave-lengths and solutions are given in the following list :—

λ .	Solution			D (water).
	A.	B.	C.	
4350	1	1	1	1
4047	1	1	1	1
3652	1	1	1	1
3341	3	3	2	1
3128	—	5	3	2

The exposures were automatically timed with the aid of a clock which operated the light shutter by means of a simple but effective electromagnetic device. During the taking of the plates no attempt was made to control the constancy of the mercury arc, as we found by experiment that the arc, when allowed to burn in for 75 minutes, remained sufficiently steady in spite of rapid fluctuations on the mains. This constancy of the source was revealed by the perfect symmetry of the graphs deduced from the plates, provided that the precaution was taken of allowing the plates to remain undeveloped for a sufficient time.

The density of the images recorded on the plates was measured by means of a Moll microphotometer, which we slightly modified for our purpose. The galvanometer deflexions were observed visually. In all cases we observed the deflexion corresponding to the maximum density of the image. During these observations the microphotometer source of light was left undisturbed, as attempts to control the current passing through its filament did not meet with any success. So long as the batteries supplying the current were freshly charged,

we found, on waiting for several minutes after making the current, that its subsequent variation was seldom more than 1 to 2 parts in 400.

Data concerning the accuracy of the photographic observations are given in Table II. in which are recorded the results for solution B. The first column refers to the interval between the analyser settings in degrees, and the second column to the region omitted in the neighbourhood of the extinction position. The choice of these values was such as to enable observations to be made on the steep portion of the curve formed by plotting the microphotometer deflexion against analyser setting. The columns labelled "In" and "Out" refer to the

TANLE II.

Analyser interval (in degrees).	Gap (in degrees).	Exposure (in min.).	λ (in Å.).	In.	Out.	Z.	R (in degrees).	Possible error (in degrees), \pm .
.15	.6	1	4350	17.253	3.518	20.771	13.735	.006
.25	1.0	1	4047	18.288	2.513	20.801	15.775	.013
.25	1.0	1	3652	19.755	0.998	20.753	18.757	.020
.75	3.0	3	3341	20.763	0.032	20.795	20.731	.058
2.00	24.0	5	3128	19.82	0.93	20.75	18.89	.40

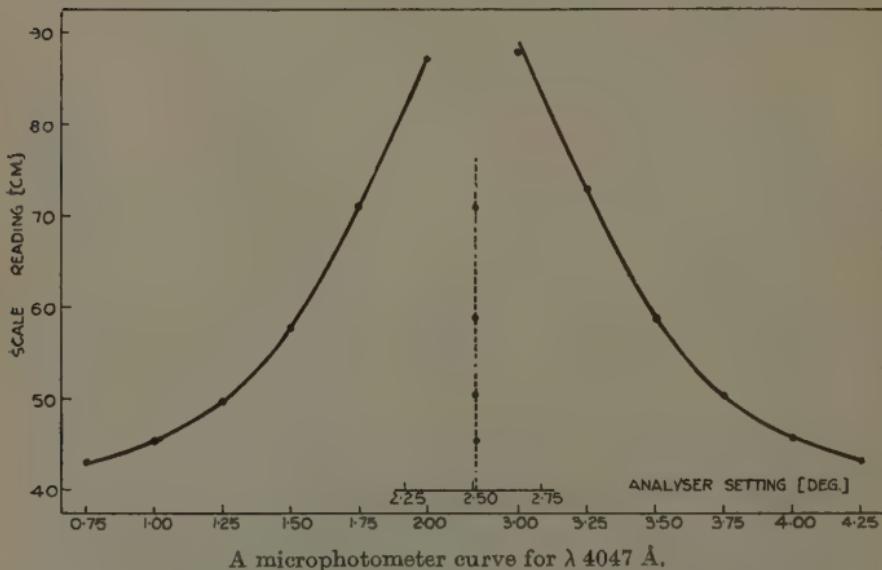
positions of the commutator giving the two senses of the current through the electromagnet. In these columns are given the extinction positions, as deduced from the axis of symmetry of the corresponding microphotometer curve. The number under Z gives the sum of the readings for the extinction positions in the "In" and "Out" positions.

Provided that no shift in the polarizer has taken place, *cæteris paribus*, this sum should be constant within the limits of error for all the wave-lengths. This Z value serves as a useful control for testing the correctness of the readings. The column labelled R gives the rotation and the last column the possible error in the rotation, as deduced from the microphotometer curve. This possible error has been taken as the sum for the "In"

and "Out" plates of the half widths of the intervals in which the points used to trace the axes of symmetry lie. The probable error will be, of course, certainly less than this possible error. Fig. 3 gives the "Out" position curve for wave-length 4047 Å. for solution B. As a rule, we found that the possible error in any extinction position was of the order of one-twentieth of the interval between the analyser settings.

Bruhat and Pauthenier * have made a very complete analysis of the errors arising in their photographic method. They show that the main source of error arises from the

Fig. 3.



imperfection of the quartz end plates cut perpendicular to the optic axis, which are necessary at the present time for observations in the quartz region of the ultra-violet. Our preliminary observations were made with a pair of well worked plane and parallel balanced quartz end plates. These plates were mounted at such an angle that the light, multiply reflected within the cell, just missed passing through the slit of the spectrograph. It was found, however, that the elliptical polarization produced by the passage of the light in a non-axial direction spoiled the precision of the method. The angle between the plates

* *Loc. cit.*

could have been reduced by the employment of a longer focus lens L_3 , but this would have prolonged the exposures intolerably. We therefore avoided the use of crystalline quartz and decided that, as the cerium solutions already absorb strongly in the neighbourhood of wave-length 3128 Å., a pair of glass plates would serve our purpose. These glass plates were set at an angle of .6 minutes. Under this condition no effect due to multiple reflexion was observed, the spectral lines having a uniform appearance.

TABLE III.
Observed Rotations in Degrees.

λ in Å.	Solutions.				Water.	End plates.
	A.	B.	C.	D.		
5893	—	—	—	—	10.123	2.032
5780	6.442	7.790	8.949	10.596	10.597	2.119
5461	7.150	8.702	10.046	11.943	11.953	2.412
4350	—	—	—	—	19.797	4.018
4350	10.70	13.735	16.31	19.89	19.95	4.065
4047	11.99	15.775	19.03	23.52	23.585	4.81
3652	13.28	18.76	23.425	30.00	30.02	6.16
3341	12.65	20.73	27.59	37.27	37.32	7.62
3128	—	18.89	29.52	44.00	44.12	9.04

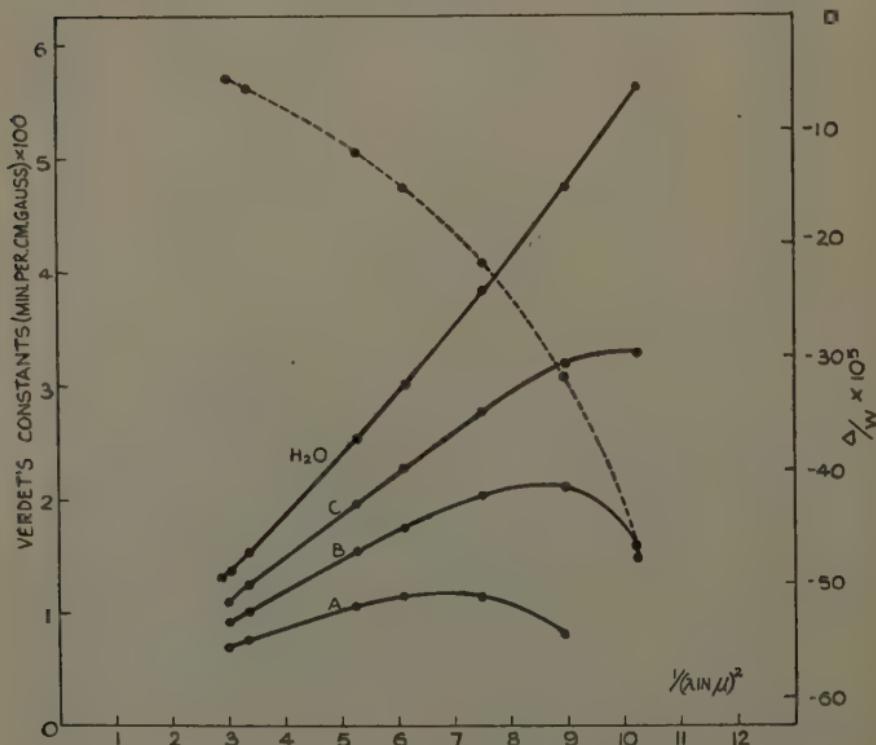
Table III. gives the observed rotations (including the effect of end plates) for the solutions and water, together with the end plate rotations. The results above the division refer to the visual observations, while those below it refer to the photographic observations. The presence of two values for wave-length 4350 Å., has already been explained. Taking Rodger and Watson's value * for the Verdet constant of water at 22.2° C. for wave-length 5893 Å., to be 0.01308' per cm. gauss, the observations have been reduced to Verdet constants, the values of which are given in Table IV., and in graphical form in fig. 4.

* *Phil. Trans. A.* clxxxvi. p. 621 (1895).

TABLE IV.
Verdet Constants (min. per cm. gauss).

λ in Å.	Cerous sulphate solutions.			Lanthanum sulphate. D.	Water.
	A.	B.	C.		
5893	—	—	—	—	·01308
5780	·00699	·00917	·01104	·01371	·01371
5461	·00766	·01017	·01234	·01540	·01542
4350	·01065	·01552	·01964	·02540	·02550
4047	·01153	·01761	·02281	·03002	·03013
3652	·01144	·02022	·02771	·03826	·03830
3341	·00808	·02104	·03206	·04757	·04766
3128	—	·01581	·03286	·05610	·05630

Fig. 4.



The dispersion of the magnetic rotation and the "specific rotation" (Δ/W) of cerous sulphate solutions.

Since the above was written data concerning the magnetic rotatory dispersion of water in the ultra-violet have been published by Bruhat and Guinier *. In view

TABLE V.

λ in Å.	Roberts.	Present authors.	Bruhat & Guinier.
5893	·5136	·5137	·5160
5461	·6020	·6057	·6075
4358	·9891	—	1·000
4350	—	1·002	—
4054	—	—	1·180
4047	1·181	1·184	—
3665	1·499	—	—
3655	—	—	1·504
3652	—	1·504	—
3341	1·872	1·872	1·872
3131	2·217	—	—
3130	—	—	2·214
3128	—	2·212	—
2805	2·967	—	—
2804	—	—	2·974
2655	3·493	—	—
2652	—	—	3·488
2540	—	—	3·963
2537	3·990	—	—
2482	4·263	—	4·258

of the disagreement between published measurements of the magnetic rotation of water in the ultra-violet, we have drawn up Table V., in which the values obtained

* G. Bruhat and A. Guinier, *Compt. Rendus*, cxcvii. p. 1028 (1933).

by one of us *, our present values, and those of Bruhat and Guinier are compared. To effect this comparison, we have reduced our results by taking 1.872 as the common value for the wave-length 3341 Å. It will be seen that our photographic measurements, so far as they go, are in good agreement with those of Bruhat and Guinier, while the measurements of Roberts over a wider range are generally not very different.

V. REFRACTIVE INDEX MEASUREMENTS.

A complete study of the Faraday effect in solutions requires a knowledge of the refractive indices of the solution and solvent. For this purpose alone the refractive indices need not be known with great precision. With the object, however, of obtaining information concerning the behaviour of the cerous and sulphate ions in solution, we have obtained the refractive indices of our solutions and water to about one unit in the fifth decimal place.

In our method we have made use of the data due to Fabry and Barot † of setting the back face BC (fig. 5) of the prism ABC normal to the incident beam. We have avoided the photography of the direct slit image, which is always blurred owing to the chromatic aberration of the objectives, by using only measurements for which the collimator and telescope have been adjusted to yield parallel light. To accomplish this, we have fixed on to a geometrical slide a 60° prism consisting of three accurately plane parallel quartz plates (cut parallel to the optic axis) wrung on to an optically worked hollow block of quartz. This geometrical slide, without further adjustment, allows the prism to be moved over into the symmetrical position (shown dotted in fig. 5) with respect to the incident beam. In both positions the whole available aperture of the prism could be used, and thus no loss in resolving power was entailed.

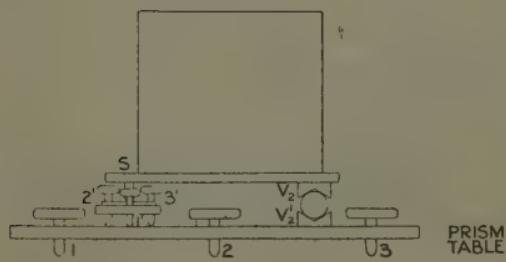
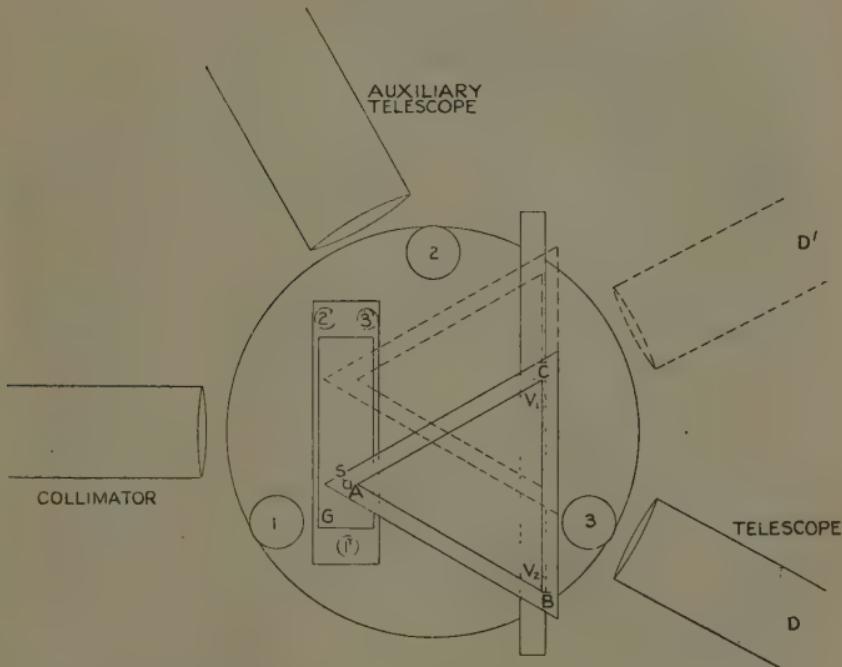
The telescope positions, D, D' were chosen so that the particular line under examination in the left and right spectra occupied nearly the same position on the plate. The calibration of the plate measurements to give angular deviations was effected, without removal of the prism,

* R. W. Roberts, Phil. Mag. ix. p. 361 (1930).

† C. Fabry and J. Barot, Rev. d'Opt. vii. p. 429 (1928).

by simply photographing the spectrum with the angular position of the telescope differing by half a degree from the position D' . In order to avoid aberration effects, the settings of the telescope were arranged so as to bring

Fig. 5.



The prism mount.

the spectral region under consideration into the middle of the plate.

If α is the mean of the base angles of the face BC, $2 D$ the angle between the refracted rays, the refractive

index μ of the solution inside the prism may be calculated by means of the formula

$$\mu^2 = 1 + \frac{\sin^2 D}{\sin^2 \alpha} + 2 \cot \alpha \sin D.$$

The detail of the slide is given in fig. 5. The prism was waxed on to a brass plate, which carried two V grooves V_1 and V_2 , and a leg S with a hemispherical end. V_1 , V_2 rested on an accurately worked steel cylinder, which in turn rested in two V grooves, V_1' , V_2' , fixed to the prism table. The leg S made contact with an optically worked piece of glass G waxed to a plate with three levelling screws 1^1 , 2^1 , 3^1 resting in a hole, slot, and plane on the prism table.

By autocollimation effected on the face BC of the prism, it was easy, by operating on the screws 1^1 , 2^1 , 3^1 , to arrange that the plane G was parallel to the axis of the cylinder. The orientation of the prism relative to the axes of the collimator and telescope was adjusted by means of the screws 1, 2, 3, resting in three radial V grooves in the spectrometer table. During the observations the slide motion was controlled by autocollimation effected on the face AC by means of an auxiliary telescope placed as in fig. 5.

The method assumes that the base angles of the face BC are to a high degree of accuracy equal, and that the pyramidal error is small. In our prism these conditions were fulfilled.

The plates were taken in the neighbourhood of $18.0^\circ C$. The small corrections necessary to reduce the refractive indices to $18.0^\circ C$. were determined from observations of the shifts of the spectral lines when the temperature of the apparatus and its surroundings was raised through about 7 degrees centigrade.

Table VI. contains the values of the refractive indices of the solutions and water. From these values the molecular refractions of cerous sulphate and lanthanous sulphate have been calculated by means of the formula

$$\frac{1}{d_4^{18}} \frac{n^2 - 1}{n^2 + 2} = \frac{1}{d^{18}} \left(1 - \frac{W}{100} \right) \frac{n_w^2 - 1}{n_w^2 + 2} + \frac{W R}{100 M},$$

where n_w = refractive index of water at $18.0^\circ C$.

n = " " " solution at $18.0^\circ C$.

R = molecular refraction of the anhydrous salt

M = " " weight " " " "

The results of the calculations are given in Table VII., from which it will be seen that over our range of con-

TABLE VI.
Refractive Indices at 18.0° C.

λ in Å.	Solutions.				Water
	A.	B.	C.	D (La.)	
5790	1.35019	1.34493	1.34033	1.33776	1.33349
5770	1.35025	1.34499	1.34040	1.33784	1.33355
5461	1.35133	1.34613	1.34150	1.33893	1.33464
4358	1.35735	1.35206	1.34737	1.34475	1.34040
4047	1.36002	1.35466	1.34905	1.34731	1.34291
3655	1.36445	1.35905	1.35428	1.35161	1.34716
3341	1.36940	1.36390	1.35909	1.35637	1.35183
3131	—	—	1.36328	1.36050	1.35592

TABLE VII.
Molecular Refractions.

λ in Å.	Lanthanum sulphate.	Cerous sulphate.				Calculated.
		A.	B.	C.	Mean.	
5790	49.18	51.6	51.4	51.2	51.4	51.4
5461	49.40	51.5	51.6	51.4	51.5	51.5
4358	49.89	52.2	52.2	52.2	52.2	52.2
4047	50.36	52.6	52.5	52.4	52.5	52.5
3655	50.81	53.0	53.0	52.9	53.0	53.0
3341	51.70	53.7	54.0	53.7	53.8	53.6
3131	51.89	—	—	54.2	54.2	54.2

centration the molecular refraction of cerous sulphate is independent of the concentration, whereas for cobalt sulphate * there is a variation with concentration.

* R. W. Roberts, *loc. cit.*

The dispersion of the molecular refraction of cerous sulphate may be represented by means of the formula

$$R = \frac{8.281 \cdot 10^{10}}{(1.374 \cdot 10^{-5})^{-2} - \lambda^{-2}} + 34.84,$$

where λ is in cm.

The molecular refractions calculated by means of this formula are given in the last column of Table VII. The value 1374 Å. for the wave-length occurring in the dispersion formula is plainly too large, but the accuracy of the observations does not permit of the introduction of a second characteristic wave-length in the dispersion formula. Unfortunately, as little is known concerning the absorption of sulphates in the far ultra-violet it does not seem possible at present to calculate with accuracy the strength of the dispersive absorption bands of the sulphate ion.

VI. ABSORPTION DATA.

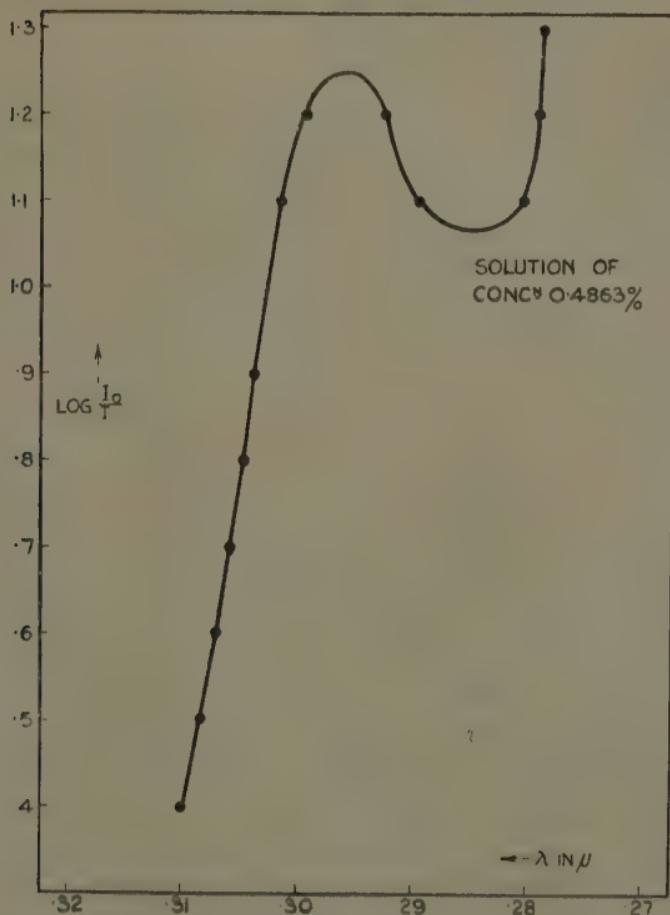
The refractivity data for cerous sulphate, as may be seen by comparison with those for lanthanous sulphate, are of no value in determining the wave-lengths of the absorption bands responsible for the magnetic rotation. In order to obtain the wave-lengths and intensities of these bands recourse must be had to direct absorption experiments. At our request Dr. R. A. Morton very kindly undertook the investigation of the absorption of two solutions provided by us. The Hilger sector method with an under water tungsten spark was used. For both solutions, one of the divided beams was compensated by a cell containing distilled water. The results of the measurements are given in figs. 6 and 7.

Fig. 6 relates to a solution of cerous sulphate of strength $W = .4863$ and density $d_4^{18} = 1.00387$, contained in a 2 cm. cell. The maximum extinction occurs at wave-length 2960 Å.

Fig. 7 shows two neighbouring absorption bands with wave-lengths 2540 and 2400 Å. This figure was obtained from a solution of strength $W = .0467$, and density $d_4^{18} = .99908$, contained in a 1 cm. cell. In addition to the above data, a further plate was taken which revealed the presence of a fourth absorption band with wave-length 2230 Å.

These bands may be reasonably attributed to the cerous ion, as they are found in cerous chloride and in various crystals containing the cerous ion. Dr. Morton has further investigated this matter, and has obtained additional evidence in favour of this assertion.

Fig. 6.



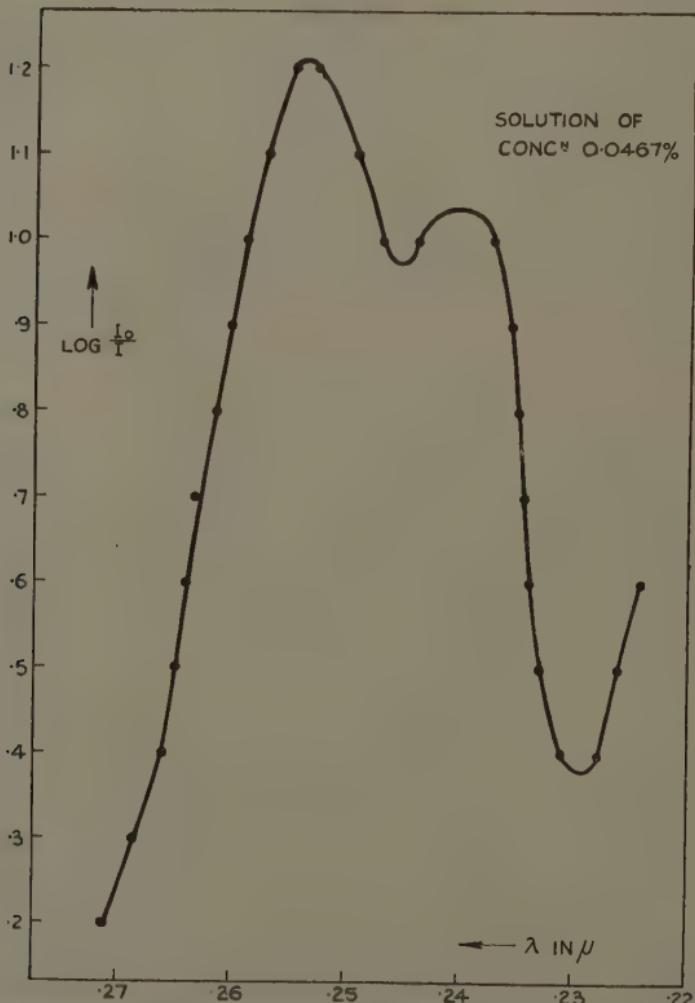
The absorption of a cerous sulphate solution in the neighbourhood of the band λ 2960 Å.

For our work we shall only be concerned with the absorption bands with wave-lengths 2960 and 2540 Å. Although these bands have each a half-width of about 200 Å., we shall treat them as narrow for the purpose of obtaining an estimate of their strengths. For narrow

bands we have the well-known formula * for the strength f of an absorption band, for which the incident light intensity I_0 is reduced to I in a length x ,

$$f = \frac{\mu_m m c v'_k}{2 N e^2} \frac{1}{x} \log \left(\frac{I_0}{I} \right)_m ,$$

Fig. 7.



The absorption of cerous sulphate solution in the neighbourhood of the bands $\lambda 2540$ and $\lambda 2400$ Å.

where the suffix m refers to the wave-length of the maximum absorption, μ_m to the refractive index of the solvent

* See, for instance, W. Kuhn, *Kgl. Vidensk. Selskab., M.-fys. Medd.* Bd. vii, Nr. 12, S. 8.

for this wave-length, ν'_k to the frequency of the half-width of the band, N to the number of absorbing atoms per c.c., while e and m refer to the charge and mass of the electron. Estimating from figs. 6 and 7 the half-widths from the long wave-length side of the absorption curves, we find

$$\text{for } \lambda 2960 \text{ \AA.}, f = 8.09 \times 10^{-4},$$

while

$$\text{for } \lambda 2540 \text{ \AA.}, f = 2.065 \times 10^{-2}.$$

VII. COMPARISON WITH THEORY.

In this section we shall apply Rosenfeld's * quantum mechanical theory of the Faraday effect in atoms to our results. This theory requires a knowledge of the ground state of the atom under consideration. In the case of the trebly ionized cerium atom the ground state has not as yet been determined with certainty.

From emission data Gibbs and White † and Badami ‡ give the ground state as a $5^2D_{3/2}$ state, while Hund's theory of spectral terms, which is well supported by susceptibility data for the rare earth ions, shows that it is a $4^2F_{5/2}$ state.

Further evidence concerning the ground state may be obtained from absorption data. Freed § interprets the absorption spectrum of the cerous ion in the ultra-violet as due to transitions from the 4^2F states to the 5^2D states. Bose and Datta || indeed find that the relative intensities of the 2960 Å. and 2540 Å. bands may be explained if these bands arise from the transitions $4^2F_{5/2} \rightarrow 5^2D_{5/2}$ and $4^2F_{5/2} \rightarrow 5^2D_{3/2}$ respectively. In a later work ¶, which has just come to hand, they assign transitions to the previously mentioned bands at 2400 and 2230 Å., which correspond to certain emission assignments given by Badami, but stand in contradiction to Freed's interpretation. In view of the uncertain spectroscopic interpretations of the 2400 and 2230 Å., bands we shall not consider them further. We shall, however, take over Bose and Datta's interpretation of the absorption bands with wave-lengths 2960 and 2540 Å.

* L. Rosenfeld, *Zeits. f. Phys.* lvii. p. 835 (1930).

† *Loc. cit.*

‡ J. S. Badami, *Proc. Phys. Soc.* xlvi. p. 53 (1931).

§ *Loc. cit.*

|| *Loc. cit.*

¶ D. M. Bose and S. Datta, *Zeits. f. Phys.* lxxx. p. 376 (1933).

According to Sommerfeld's relativity doublet formula there will be a separation between the $4^2F_{5/2, 7/2}$ levels of about 2500 cm.^{-1} , which stands in approximate agreement with the Raman effect data of Brunetti and Ollano *. Owing to the large separation between these levels we can suppose, for our purpose, even at room-temperature, that all the ions are in the $4^2F_{5/2}$ state.

Rosenfeld gives the following formula for the rotation per unit length,

$$\Theta = \frac{4\pi^2\beta}{\lambda\bar{n}},$$

where \bar{n} is the mean refractive index for left-handed and right-handed circularly polarized waves of wave-length λ , and β is proportional to the number of atoms per c.c. To avoid further explanation of the symbols we shall take over Rosenfeld's notation almost entirely. In the case of solutions we must replace \bar{n} by the expression

$$\frac{9n}{(n^2+2)^2},$$

where n is the refractive index of the solution, so that

$$\Theta = \frac{4\pi^2(n^2+2)^2\beta}{9\lambda n}.$$

Splitting β into two parts arising from the solvent and solute respectively, it is easily shown that

$$\frac{n}{(n^2+2)^2} \frac{\Theta}{d} = \frac{n_w}{(n_w^2+2)^2} \frac{\Theta_w}{d_w} \left(1 - \frac{W}{100}\right) + \frac{4\pi^2}{9\lambda d} \beta_{\text{solute}}$$

where β_{solute} now refers to the solute, the suffix w to the water, and W and d have their previous meaning. If instead of Θ 's we use Verdet constants V , it follows that the difference

$$\Delta = \frac{n}{(n^2+2)^2} \frac{V}{d} - \frac{n_w}{(n_w^2+2)^2} \left(1 - \frac{W}{100}\right) \frac{V_w}{d_w}.$$

is a quantity characteristic of the rotation of the solute.

According to the above equations Δ/W should be independent of the strength of the solution. Table VIII. contains the values of Δ/W calculated from the rotations. It will be seen that for the range of concentration used cerous sulphate solutions satisfy this condition.

* R. Brunetti and Z. Ollano, *Zeits. f. Phys.* lxxv. p. 415 (1932).

We require now to express β_{solute} in terms of atomic constants. In the case of the cerous ion the separation between the excited states $5^2\text{D}_{3/2, 5/2}$ is so large that it is necessary to use Rosenfeld's formula (68), although owing to the high working temperature, the first condition for its validity ($kT \ll \beta_l$) is not too well satisfied. We have then, on restricting our work to the two absorption bands $4^2\text{F}_{5/2} \rightarrow 5^2\text{D}_{5/2}$, $4^2\text{F}_{5/2} \rightarrow 5^2\text{D}_{3/2}$ whose frequencies

TABLE VIII.
Values of $-(\Delta/W) \times 10^5$.

λ in Å.	Cerous sulphate solutions.				Lanthanous. sulphate.
	A.	B.	C.	Weighted mean.	
5780	5.47	5.49	5.52	5.49 ± 0.04	0.13
5461	6.32	6.33	6.37	6.33 ± 0.05	0.18
4350	11.98	11.95	11.95	11.96 ± 0.06	0.42
4047	15.04	15.05	14.99	15.04 ± 0.04	0.66
3652	21.62	21.62	21.63	21.62 ± 0.08	0.54
3341	31.74	31.71	31.75	31.73 ± 0.15	0.72
3128	—	47.93	47.43	47.68 ± 0.30	1.21

we shall denote by $v^{5/2: 5/2}$ and $v^{3/2: 5/2}$ respectively, the following values for the \bar{b} coefficients :—

$$\bar{b}(\text{D}_{3/2}, \text{F}_{5/2}) = \frac{14}{5} D_{3/2}^2$$

$$b(\text{D}_{5/2}, \text{F}_{5/2}) = \frac{2}{35} D_{5/2}^2,$$

$$\bar{b}(\text{F}_{5/2}, \text{D}_{3/2}) = -\frac{28}{25} D_{3/2}^2,$$

$$\bar{b}(\text{F}_{5/2}, \text{D}_{5/2}) = \frac{2}{25} D_{5/2}^2,$$

where $D_{2/2}^3$ is proportional to the strength of these absorption bands. These b values give at once,

$$A(\text{D}_{3/2}, \text{F}_{5/2}) = \frac{42}{25} \mu_0 H D_{3/2}^2,$$

$$A(\text{D}_{5/2}, \text{F}_{5/2}) = \frac{24}{175} \mu_0 H D_{5/2}^2,$$

whence we have

$$\beta_{\text{solute}} = \frac{4N\nu\mu_0H}{h^2(2j+1)} \left\{ \frac{\nu^{5/2:5/2} \frac{24}{175}}{((\nu^{5/2:5/2})^2 - \nu^2)^2} + \frac{\nu^{3/2:5/2} \frac{42}{25}}{((\nu^{3/2:5/2})^2 - \nu^2)^2} \right\} D_3^2$$

$$- \frac{2N\nu\mu_0H}{kTh(2j+1)} \left\{ \frac{\frac{2}{35}}{(\nu^{5/2:5/2})^2 - \nu^2} + \frac{\frac{14}{5}}{(\nu^{3/2:5/2})^2 - \nu^2} \right\} D_3^2$$

which gives, on inserting the value $j=5/2$,

$$\frac{\Delta}{W} = \frac{4\pi^2\mu_0c}{27h} \frac{N}{Wd} \frac{1}{\lambda^2} \times$$

$$\left\{ \frac{48}{175h} \frac{\nu^{5/2:5/2}}{((\nu^{5/2:5/2})^2 - \nu^2)^2} + \frac{84}{25h} \frac{\nu^{3/2:5/2}}{((\nu^{3/2:5/2})^2 - \nu^2)^2} \right.$$

$$\left. - \frac{1}{kT} \frac{2/35}{(\nu^{5/2:5/2})^2 - \nu^2} - \frac{1}{kT} \frac{14/5}{(\nu^{3/2:5/2})^2 - \nu^2} \right\} D_3^2$$

where N is the number of Ce^{+++} ions per c.c. of solution.

Using the experimental values of Δ/W , we have calculated the value of D_3^2 for each line. If the assumptions involved in deriving the above expression for Δ/W are true, then D_3^2 should have the same value for each wave-length within the limits of experimental error. Table IX. shows that this is the case for all wave-lengths except 3128 Å. If, owing to the stronger absorption of light of wave-length 3125 Å. than that of wave-length 3132 Å. in cerium solutions, we take, instead of 3128 Å., a centre of gravity wave-length greater than 3128 Å., the calculated value of D_3^2 is diminished. As this process, for any reasonable assumed wave-length still gives a value of D_3^2 greater than the remaining ones, further absorption bands must be taken into consideration. Owing to the uncertain spectroscopic data for absorption bands other than 2960 Å. and 2540 Å., we have not pursued this matter.

So far we have made no correction for the rotation due to the sulphate ion. It was expected that this correction could be found from observations of the magnetic rotation of lanthanous sulphate in solution. According to Table VIII. the Δ/W value for solution D is negative, indicating the presence of a paramagnetic rotation. As this rotation is too large to be attributed to cerium impurities in our lanthanous sulphate, we must conclude that, although the ground state of La^{+++} is an S state, La^{+++} gives rise to a paramagnetic rotation. According to theory this would occur if the excited states of La^{+++} possessed such large energy separations that, as with Ce^{+++} , the effect of the inner quantum number of the excited states must be taken into consideration.

TABLE IX.
Values of $D_3^2 \times 10^{37}$.

λ in Å.	D_3^2 .
5780	6.49 ± 0.05
5461	6.49 ± 0.05
4350	6.53 ± 0.04
4047	6.53 ± 0.02
3652	6.50 ± 0.02
3341	6.49 ± 0.03
3128	6.80 ± 0.10
Weighted mean (omitting 3128).	6.515

As the magnetic rotatory dispersion¹ of cerous sulphate throughout the range 5780–3341 Å is satisfactorily explained without taking into account the correction for the sulphate ion, we conclude that this correction must be very small. This is in agreement with the dispersion data, as the effective dispersive wave-length lies in the far ultra-violet.

Knowing the value of D_3^2 we can calculate the f values for the absorption bands 2960 Å. and 2540 Å.

The quantum expression for the f factor occurring in the absorption equation of section VI. is

$$f_{ij'} = \frac{8\pi^2 m \nu^{(j'j)}}{e^2 \hbar (2j+1) \sum_{m'm} |X_{m'}^{(j'j)}|^2}$$

where $X_{m' m}^{ij}$ is an element of the electric moment matrix. Evaluating the summation we find

$$f_{3 \frac{5}{2}}^{2 \frac{5}{2}} = \frac{64\pi^2 m \nu^{(5/2, 5/2)}}{3e^2 h} \frac{D_3^2}{60},$$

$$f_{3 \frac{5}{2}}^{2 \frac{3}{2}} = \frac{64\pi^2 m \nu^{(3/2, 5/2)}}{3e^2 h} \frac{14D_3^2}{60}.$$

These give, on taking the weighted mean value of D_3^2 as 6.515×10^{-37} ,

$$f_{2960} = 1.404 \times 10^{-3}$$

$$f_{2540} = 2.291 \times 10^{-2}.$$

These values are in fair agreement with the f values obtained from the absorption measurements given in Section VI.

Exact agreement is not to be expected, as, apart from other factors, we have been informed by Dr. R. A. Morton that Beer's Law is not satisfied by cerous solutions. As far as order of magnitude is concerned, our larger f value is in agreement with calculations made by Gorter * and Serber (quoted by Gorter *) on different grounds.

SUMMARY.

For the range of concentration used our results show that :—

(1) The "specific rotations" (Δ/W) of cerous sulphate and lanthanous sulphate are negative, and for cerous sulphate Δ/W is independent of the concentration.

(2) The magnetic rotatory dispersion of cerous sulphate throughout the wave-length range 5780–3341 Å. may be calculated by taking into account two absorption bands of wave-lengths 2960 Å. ($4^2F_{5/2} \rightarrow 5^2D_{5/2}$) and 2540 Å. ($4^2F_{5/2} \rightarrow 5^2D_{3/2}$), whose f values are 1.404×10^{-3} and 2.291×10^{-2} respectively, and therefore

(3) the ground state of the cerous ion is $4^2F_{5/2}$ (Hund) and not $5^2D_{3/2}$ (Gibbs and White).

(4) The molecular refraction of cerous sulphate is independent of the concentration.

We owe our best thanks to Prof. L. R. Wilberforce for the facilities and apparatus placed at our disposal ;

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We also wish to record here our indebtedness to the late Mr. J. M. Barkla, M.Sc., who was associated with us in some preliminary refractive index determinations.

The George Holt Physics Laboratory,
The University, Liverpool.
December 14, 1933.

LXXXIII. The Theory of the Paramagnetic Rotation and Susceptibility in Manganous and Ferric Salts. *By Prof. J. H. VAN VLECK, Professor of Physics at the University of Wisconsin, and Dr. W. G. PENNEY, Senior Student of the 1851 Exhibition, Trinity College, Cambridge *.*

1. THE CRYSTALLINE SPLITTING OF 6S STATES.

IN salts of the iron group the orbital angular momentum is largely frozen out by crystalline fields, in accordance with known theoretical principles ⁽¹⁾. The residual orbital angular momentum is, however, of cardinal importance in explaining magnetic anisotropy, departures from Curie's law, and, in fact, any deviation of the susceptibility from the "spin-only" value,

$$\chi = 4N\beta^2S(S+1)/3kT. \quad . \quad . \quad . \quad (1)$$

Here β is the Bohr magneton $he/4\pi mc$ and S is the spin quantum number.

The ions Mn^{++} and Fe^{+++} differ from others of the iron group in that they are in 6S states, and so devoid of angular momentum if there is ideal Russell-Saunders coupling. Hence these ions should be much more isotropic and conform closer to (1) than is usual with the members of this group. This is borne out by the experimental evidence. Thus, for example, Rabi ⁽²⁾ finds that the magnetic anisotropy of $MnSO_4(NH_4)_2SO_4 \cdot 6H_2O$ at room-temperatures amounts to about $\frac{3}{4}$ of 1 per cent., as compared with 30, $1\frac{1}{2}$, and 20 per cent. for the ammonio-sulphates of divalent Co, Ni, and Cu respectively.

* Communicated by the Authors.

The aim of the present paper is to consider why (1) should not be a perfect approximation in manganous salts. Experimentally, deviations from (1) in Mn^{++} are evidenced not only by the existence of some anisotropy, though small, but also by departures from Curie's law at very low temperatures. The conclusions we shall obtain can be applied directly to the ferric ion, but as the experimental data here are not as complete as those with manganese, we confine our attention mainly to the latter ion.

One reason why the susceptibilities of solid manganous compounds should not have the value (1), characteristic of free ions in S states, is provided by the Heisenberg exchange effect. It is well known that this effect makes the denominator of (1) become $T + \Delta$ instead of T. The exchange coupling is, however, incapable by itself of giving any magnetic anisotropy. Also this coupling cannot be of dominant importance in materials of considerable magnetic dilution, such as, for example, the ammonosulphates. Only the exchange integrals connecting two paramagnetic ions have any hindering effect on the orientation of the spin, and in such materials the spacing between these ions is extremely large. In fact, oftentimes the magnetic spin-spin coupling between paramagnetic atoms, which depends on their separation r in the fashion r rather than e^{-ar} , may actually be more important than exchange effects if the dilution is considerable. Such interatomic magnetic interaction is, however, doubtless too small to account for most of the departures from (1) in hydrated salts, for it is, presumably, of about the same order of magnitude in hydrated rare earth and iron salts, and the classic Leiden experiments on $Gd_2(SO_4)_3 \cdot 8H_2O$ show that in the former there is no appreciable interference due to this cause even at the temperature of liquid helium.

We believe that the true explanation of the deviations from (1) in dilute manganous salts is found when higher order approximations are considered in connection with the crystalline potential used by Kramers, Bethe, Van Vleck, Penney, and Schlapp⁽¹⁾. In the compounds which we shall consider, this field is probably dominantly cubic, so that its potential is approximately

$$V_{\text{crys.}} = Ax^2 + By^2 + Cz^2 + D(x^4 + y^4 + z^4), \dots \quad (2)$$

if the lowest powers in a Taylor's development in x, y, z are the most important. Here the terms of second degree are the rhombic ones, and are subordinate in importance to the fourth degree or cubic ones. It is not unlikely that the convergence of the Taylor's development is poor, so that higher powers than written in (2) are important, but this will not affect the results of the present paper, as our applications are contingent primarily only upon the group-properties of crystalline "covering" operations, and we give (2) simply to have a concrete illustration of a nearly cubic crystalline potential.

Theory.—Let us suppose that the wave-equation for a free Mn^{++} ion has been solved with neglect of spin-orbit forces. Our unperturbed wave-functions then represent perfect Russell-Saunders quantization. Introduce as a perturbing potential

$$H_1 + H_2 = V_{\text{crys.}} + \sum_i a_i \mathbf{l}_i \cdot \mathbf{s}_i.$$

Here H_1 is the crystalline potential, and H_2 the part of the Hamiltonian function arising from spin-orbit coupling within the ion. We shall introduce the notation H_r , H_m , H_c for the rhombic, monoclinic, and cubic portions of H_1 . The monoclinic part is needed only if there is less than rhombic symmetry, and does not enter, for instance, with the potential (2). If we make the usual approximation of retaining only diagonal terms in L, S , then (3) will give no Stark separation for any S level, and no deviation of the susceptibility from (1). The situation is, however, different when higher approximations are considered. Neither H_1 nor H_2 , acting alone, is capable of splitting an S state in any approximation, but the interplay of H_1 and H_2 will give the desired separation. In other words, simultaneous correction for the crystalline field and incipient j - j coupling will divide the 6S level. This is fairly obvious on physical grounds, since with any trace of j - j coupling an S state no longer has a centro-symmetric charge distribution. A surer proof that (3) will separate 6S is provided by group theory. Bethe's group methods⁽³⁾ show that $J=5/2$ contains three different two-fold representations of the rhombic group, and one four-fold and one two-fold representation (Γ_6, Γ_7 in his notation) of the cubic group. Hence when both terms of (3) are retained, and the calculation is

carried far enough, we can feel sure that our 6S state will separate into three distinct levels in a rhombic field, and into but two in a perfectly cubic one. The inevitable presence of the Kramers two-fold degeneracy ⁽⁴⁾ in systems with an odd number of electron makes it clear that a separation into more than three levels cannot possibly be achieved by (3), regardless of how little symmetry there is in the crystalline potential.

How far the perturbation calculation, consisting of a series development in ascending powers of H_1 , H_2 , must be carried before a splitting of 6S can be secured depends upon the type of symmetry of the crystalline potential, and upon whether or not we confine our attention to those matrix elements of H_1 , H_2 which are interior to the configuration $3d^5$. An example of an interior element of H_2 is $H_2(3d^5\ ^6S; 3d^5\ ^4P)$; a typical, more general element is $H_2(3d^5\ ^6S; 3d^4m d\ ^6P)$. ($m > 3$). The results appear to be as summarized in the following table :—

I. Secular problem restricted to multiplets arising from the configuration d^5 .

(a) Cubic symmetry :

$$h\Delta\nu \sim [H_2]^3[H_c]^2/h^4\nu_I^4 \sim 1 \text{ cm.}^{-1}.$$

(b) Rhombic symmetry, or less :

$$h\Delta\nu \sim [H_2]^2[H_r]/h^2\nu_I^2 \sim 1 \text{ cm.}^{-1}.$$

II. No restriction.

(a) Cubic symmetry :

$$h\Delta\nu \sim (H_2)^2(H_c)^2/h^3\nu_{II}^3 \sim 01 \text{ cm.}^{-1}.$$

(b) Rhombic symmetry :

$$h\Delta\nu \sim (H_2)^2(H_r)/h^2\nu_{II}^2 \sim 01 \text{ cm.}^{-1}.$$

(c) Less than rhombic symmetry :

$$h\Delta\nu \sim (H_2)(H_m)/h\nu_{II} \sim 1 \text{ cm.}^{-1}.$$

Here ν_I denotes the order of magnitude of the frequency interval, separating the different multiplets belonging to d^5 , while ν_{II} relates to the interval between d^5 and "exterior" states, wherein an electron is excited. Presumably ν_I is considerably smaller than ν_{II} , and that is one reason why

we differentiate between I. and II. The orders of magnitude of the matrix elements of H which are and of those which are not interior to d^5 are denoted respectively by $[H]$, (H) .

We shall not give the detailed derivation of the above expressions for $h\Delta\nu$. They are obtained by inspection of the successive approximation formulæ of perturbation theory with account taken of the fact that the matrix elements of H_1 , H_2 vanish unless certain selection principles are satisfied. For instance, the matrix element of H_1 vanishes unless the initial and final state have the same multiplicity and contain the same representation of the appropriate crystallographic symmetry group. The elements of H_2 obey the selection rule

$$\Delta L=0, \pm 1; \Delta S=0, \pm 1.$$

As an illustration of the procedure we may observe that the perturbation formula for the second-order energy is

$$\Delta W = \sum_j H(ij)H(ji)/h\nu(ij).$$

We are interested only in the interplay between H_1 and H_2 , so that here $H(ij)$ must relate to H_1 and $H(ji)$ to H_2 , or *vice versa*. In order for the corresponding part of ΔW not to vanish it is necessary that H_1 and H_2 simultaneously have non-vanishing elements connecting i and j . In our problem i means the ground state 6S . Hence $H_2(ij)$ vanishes unless j is an S or P state. The case that j is an S state is trivial, since it does not contribute any properties not found in the ground state. Furthermore, a rhombic or cubic H_1 cannot have matrix elements joining S and P states, because P levels and S levels do not have any representations of the cubic or rhombic groups in common. Hence in the above tabulation a splitting is found in the second approximation only when there is less than rhombic symmetry. That the separation appears as a higher approximation in I. and II. is because 6S is the only sextet belonging to the configuration d^5 , and so H_1 is unable to yield matrix elements joining 6S with the other multiplets of d^5 . The fact that a rhombic or cubic potential leads to a separation only when quite high approximations are considered is a consequence of two circumstances. One is that the matrix elements of the orbital angular momentum always

vanish if both the initial and final states belong to Bethe's cubic representation Γ_1 , or to the corresponding identical rhombic representations. The other circumstance, important in case I. (a), is that a purely cubic field, when not supplemented by spin-orbit forces, is incapable of separating the three spatial members of a P state.

It is to be cautioned that the above formulae for $h\Delta\nu$ are only tentative, since it is conceivable that explicit calculation might reveal that for special reasons the terms of listed orders might vanish.

We may form a very rough numerical estimate of the various contributions to the splitting by taking

$$H_c \sim 10^4, H_r \sim 10^3, H_m \sim 500, h\nu_I \sim 2 \times 10^4, \\ h\nu_{II} \sim 10^5, H_2 \sim 500. \quad . \quad (4)$$

These values of H_c , H_r are obtained from Schlapp and Penney's calculations on Ni, Co⁽¹⁾. We have taken H_m to be somewhat less than H_r , because even in the monoclinic hydrated sulphates the rhombic terms are probably more important than the terms giving the departures from rhombic symmetry. The estimates of $h\nu_I$, $h\nu_{II}$ have been derived from the existing data on the spectra of Cr^+ and Mn^{++} . The choice $H_2 \sim 500 \text{ cm.}^{-1}$ is suggested by the multiplet separations observed for the configuration d^5 of Cr^+ , which is isoelectric with Mn^{++} . The corresponding separations in Mn^{++} are not available, but would be of nearly the same order of magnitude. In this connexion we must notice that in d^5 the d shell is half complete, and so there are no multiplet separations in the first approximation⁽⁵⁾; consequently multiplet intervals are of the order $[H_2]^2/h\nu_{II}$ rather than H_2 as usual. Substantially the same value for H_2 could also be obtained by interpolating between adjacent atoms in the configurations d^4 and d^6 , where the multiplets have widths of the usual order H_2 . The fact that, according to (4), the ratio $H_c/h\nu_I$ is so near unity means that the cubic portion of the crystalline field is almost able to destroy the couplings of the $\mathbf{1}$ vectors to a resultant \mathbf{L} , as one of us will discuss more fully elsewhere⁽⁶⁾. Since $H_c/h\nu_I$ is not small, the perturbation development in this ratio has an exceedingly poor convergence, but this does not affect estimates of numerical magnitudes, which depend largely on the power to which H_2 is raised.

The use of (4) yields the numerical estimates given at the end of each line in the preceding tabulation of the various contributions $h\Delta\nu$ to the Stark splitting. These estimates should be considered reliable only to within a factor 10 or so. We may conclude that the Stark separation of 6S should be at most a matter of a few cm.^{-1} . One fact is interesting, namely, that the rhombic terms usually enter in lower approximations than the cubic ones. Hence it is possible for the "rhombic" splitting to be of the same order of magnitude as the "cubic," even though the former is much smaller than the latter in the usual case (*e. g.*, Co^{++} , Ni^{++} , Cu^{++}) of ions having $L>O$.

2. THE MAGNETIC SUSCEPTIBILITY OF MANGANOUS SALTS.

Let us suppose that the perturbation problem presented by (3) has been solved except for the secular portion connected with the lifting of the degeneracy with respect to the magnetic quantum number M ⁽⁷⁾. Let a magnetic field be applied along the z -axis, which we may take as the axis of the M system of quantization. If the crystalline potential has at least rhombic symmetry, and if the z direction be one of the rhombic axes, the matrix elements of the Hamiltonian function will involve only transitions wherein M changes by an even number of units, and the secular problem connected with removal of the M degeneracy will be of the following structure for a 6S state:—

$$\begin{vmatrix} -(a+b)+5\beta\mathbf{H}-W & c & d \\ c & a+\beta\mathbf{H}-W & e \\ d & e & b+3\beta\mathbf{H}-W \end{vmatrix} = 0. \quad (5)$$

Here the determinant involves the components $M=5/2$, $1/2$, $-3/2$ of 6S . There is also another equation which involves $-5/2$, $-1/2$, $3/2$, and which is identical with (5) except that the signs of the terms proportional to $\beta\mathbf{H}$ are everywhere reversed. The discussion in the preceding section shows that the terms a , b , c , d , e , all owe their existence to the interplay of the crystalline potential and spin-orbit coupling, and are probably at most only a few cm.^{-1} in magnitude. If the crystalline field has perfect cubic symmetry, then one finds

$$c=e=0; \quad 3a=-2b=6d/5,$$

making two of the roots of (5) equal when $\mathbf{H}=0$.

The calculation of the susceptibility is greatly facilitated by the fact that, unlike the usual case $L>0$, the crystalline splitting is small compared with kT . This means that, except at the very lowest temperatures, there will be excellent convergence if the partition function and hence the susceptibilities are developed in descending powers of T . For ordinary purposes we may content ourselves with the first two terms in the development. To this approximation the three principal susceptibilities are

$$\chi_x = \frac{35N\beta^2}{3k} \left[\frac{1}{T} - \frac{r+s}{T^2} + \dots \right], \quad \dots \quad (6a)$$

$$\chi_y = \frac{35N\beta^2}{3k} \left[\frac{1}{T} - \frac{r-s}{T^2} + \dots \right], \quad \dots \quad (6b)$$

$$\chi_z = \frac{35N\beta^2}{3k} \left[\frac{1}{T} + \frac{2r}{T^2} + \dots \right], \quad \dots \quad (6c)$$

with

$$r = \frac{12a+8b}{35k}, \quad s = \frac{4c(10)^{\frac{1}{2}}+12e(2)^{\frac{1}{2}}}{35k}. \quad \dots \quad (7)$$

The above formulæ are consequences of the fact that the ratio C_2/C_1 of the coefficients of T^{-2} and T^{-1} in the development of the susceptibility is in general⁽⁸⁾ given by

$$k \frac{C_2}{C_1} = \frac{\text{Spur } HK^2}{\text{Spur } K^2} - \text{Spur } H, \quad \dots \quad (8)$$

if we write the Hamiltonian function as $H+HK$. The coefficient of T^{-1} has, of course, the usual Bose-Stoner value $4S(S+1)\beta^2/3k$ for all three axes. In (5) the Hamiltonian matrix is written in a form which permits the easy application of (8) to the derivation of the formula (6c) for the z component of susceptibility. The proof of (6a) and (6b) from (8) is slightly more complicated. It is effected either by examination of how the constants a, b, c, d, e , transform under a permutation of axes, or else by use of the formulæ for the x and y components of moment in a system of representation which diagonalizes the z component.

From the three relations (6) one sees that the coefficient of T^{-2} vanishes in the formula for the mean or "powder" susceptibility $(\chi_x + \chi_y + \chi_z)/3$. A similar result has also been found in other cases in the papers of Penney and

Schlapp⁽⁹⁾. Since the convergence of the development in $1/T$ is good in the particular case of S states, one should expect the mean susceptibility to obey Curie's law with unusual precision in manganous and ferric salts which are of sufficient dilution to permit neglect of the exchange effect. This appears to be substantiated by the existing experimental measurements⁽¹⁰⁾.

The behaviour of the individual principal susceptibilities is, of course, more interesting than that of the powder, but, unfortunately, there is a dearth of reliable data over a sufficiently wide temperature-range to test the formulæ (6). Even if such data were available, one could not use (6) to evaluate the constants of the crystalline field, except for the particular combinations (7). Considerable information, might, however, be deduced if the temperature were reduced so low that more terms are needed than given in (6), as then the constants would not be involved only in the combinations (7).

In any case one conclusion may be drawn from (6), viz., that there is an intimate connexion between the anisotropy at room-temperatures and the amount of deviation which the individual principal susceptibilities should show from Curie's law, since knowledge of anisotropy at any one temperature permits evaluation of the constants r, s . Unfortunately, as we shall see, existing data are inadequate to test even this simple prediction.

MnSO₄(NH₄)₂SO₄ · 6H₂O.—Most of the existing measurements are on manganese ammonium sulphate, which is a good salt to study because of its high magnetic dilution. Jackson and de Haas⁽¹¹⁾ have measured the principal susceptibilities at the temperatures of liquid hydrogen, while Rabi⁽²⁾, Jackson⁽¹²⁾, and Krishnan, Chakrovorty, and Banerjee⁽¹³⁾ have done so at room-temperatures. Krishnan⁽¹⁴⁾ found a computational error in the work of Jackson and de Haas, but even with the corresponding revision their data indicated a very considerable anisotropy, over 25 per cent., at the hydrogen temperatures (14–20°). We therefore made calculations to test whether this large anisotropy could be reconciled with Rabi's observation that the anisotropy at room-temperature is less than 1 per cent. These unpublished calculations used the accurate exponential forms, and so included higher powers of $1/T$ than (6), but the resulting

corrections to (6) were not particularly important even in the hydrogen range. The outcome of the calculations is that the large anisotropy found by Jackson and de Haas at low temperatures is incompatible with an anisotropy of less than 1.2 per cent. at room-temperatures, whereas Rabi finds only .75 per cent. After completion of the calculations, the situation was considerably modified by new experimental developments. Krishnan, Chakrovorty, and Banerjee (13) now claim that the anisotropy at room-temperatures is less than .1 per cent. This contention is based on a special experimental technique which they have devised for feebly anisotropic materials, and so seems rather convincing. Also, in a new paper, Jackson (12) finds that the anisotropy at room-temperatures is not over about 1 per cent., but he thus only gives an upper limit. According to (6), the anisotropy at 14° K. can be about twenty times as great as at room-temperatures, and so cannot be nearly as high as the values, 25 per cent. or so, reported by Jackson and de Haas if we accept the new measurements of Krishnan or even those of Rabi. This dilemma is removed by Jackson's (12) recent repudiation of the older work of Jackson and de Haas, which he states gave excessive anisotropy because of crystalline imperfections. Large crystals had to be used by Jackson and de Haas, and such crystals are particularly liable to flaws. New measurements on the anisotropy of manganese ammonium sulphate would thus be most welcome both at low temperatures, where there are no longer any accepted data, and at room-temperatures, where there is controversy. Theoretical considerations on the magnitude of the crystalline splitting given in the preceding section do not suffice to decide between the two values .1 and .75 per cent. reported for the anisotropy at room-temperatures, as, according to (6), even an anisotropy of .75 per cent. demands a crystalline splitting of only a very few wave-numbers. The value .1 seems slightly more plausible, as then the splitting can be less than 1 cm.⁻¹. According to Jackson, the individual susceptibilities follow Curie's law over the interval 80–292° K. with an error of less than 1 per cent. This suggests that the lower of the two estimates for the anisotropy at room-temperatures is more nearly correct, for according to (6) one would expect the Curie constants at 80° and 292° to differ by somewhat over 1 per cent. if the anisotropy

is .75 at 292°K. The excess over 1 per cent. is, however, not great enough to make this argument conclusive.

Other Manganous Salts.—In $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ Jackson⁽¹²⁾ finds that the deviations of one of the principal susceptibilities from Curie's law in the interval 80–290°K. correspond to a constant Δ about 2 in the Weiss-Curie formula

$$\chi = C/(T + \Delta).$$

The older measurements of Onnes and Oosterhuis⁽¹⁵⁾ on the powder susceptibility of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ are fitted excellently throughout their entire range 14–289°K. if one uses (6) with $\Delta 1.2^\circ$. Hence it appears that the deviations from Curie's law are of about the same order of magnitude for the individual and powder susceptibilities. This suggests that in $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, these deviations are due more to the exchange effect than to the crystalline field, for (6) shows that without exchange effect the departures should largely cancel out in the mean χ involved in the powder. Indeed, it is impossible to impute to a pure crystalline field as large a deviation of the *mean* susceptibility from Curie's law as that found by Onnes and Oosterhuis unless the crystalline splitting is made unreasonably large. It is possible for exchange effects to enter in $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and not in $\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, since in the latter the magnetic dilution is larger.

In anhydrous MnSO_4 and MnCl_2 the deviations from Curie's law are doubtless due primarily to the exchange effect. The constant Δ has the value 24 for MnSO_4 , but, rather curiously, the value 0 for MnCl_2 , provided in either case we seek to represent the susceptibility^{(16), (17)} down only to about 65°K. Below this temperature the dependence on T is too complicated to be capable of representation by (6). The crystalline structure of MnCl_2 is known, and shows that there are six Cl atoms around each Mn^{++} ion. Possibly the screening by these other atoms explains the validity of Curie's law above 65°K. or so in MnCl_2 . In MnSO_4 the number of Mn ions per c.c. is somewhat less than in the chloride, but conceivably the Mn ions are unevenly spaced, so that the minimum Mn-Mn separation is smaller than in the chloride⁽¹⁶⁾.

Variations in the Curie Constant.—The empirical effective Bohr magneton number is defined in terms of the observed susceptibility χ by the relation

$$n_B = \sqrt{\frac{3kT\chi}{N\beta^2}} \dots \dots \dots \quad (10)$$

Sometimes, even when Curie's law is valid in manganous or ferric salts, the measurements yield an effective magneton number perceptibly different from the theoretical value $n_B = [4S(S+1)]^{\frac{1}{2}} = 35^{\frac{1}{2}} = 5.92$ appearing in (1). In the case of $MnCl_2$, for instance, the empirical value is 5.61. One is thus prompted to examine what possible theoretical causes there can be for such discrepancies. Before doing so we must remember that oftentimes the experimental error in absolute susceptibilities is quite considerable, due to difficulties in calibration and to crystalline imperfections. Jackson⁽¹²⁾ notes that with strained or cracked crystals the effective magneton number of $MnSO_4(NH_4)_2SO_4 \cdot 6H_2O$ is about 3 per cent. lower than theory or the values obtained with his best crystals. In consequence he suggests that the low values reported by Rabi may be due to crystal imperfections. Jackson⁽¹²⁾ reports the following values for good crystals of various salts :

$MnSO_4(NH_4)_2SO_4 \cdot 6H_2O$	$MnSO_4 \cdot 5H_2O$	$MnSO_4 \cdot 4H_2O$
5.90	5.94	5.86
$Fe(CH_3COCHCOCH_3)_3$	$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	
5.98	5.94.	

In each of these cases the agreement with the value 5.92 seems adequate.

Two possible theoretical causes of deviation from 5.92 are the following :—

(a) Even in the free gaseous state the Mn^{++} or Fe^{+++} ions should not have a magneton number exactly equal to the Hund value 5.92, because of the fact that there is never ideal Russell-Saunders coupling, owing to distortion by spin-orbit forces. One can show that this distortion will alter the magneton number by a factor $1+q_a$, where q_a is of the order $[H_2]^2/h^2\nu_1^2$ in the notation used in section 1. If one uses the values given in (4) then q_a is only about 10^{-3} .

(b) The crystalline potential intermingles states of different L , and this may cause a distortion factor $1+q_b$, where q_b is of the order $(H_m)^2/h^2\nu_{II}^2$. With (4) this gives $q_b=10^{-5}$, a value too small to be of any consequence, but we must remember that the estimate (4) of H_m may be too low, because the matrix elements of H_m are larger for transitions between normal and excited states than for the normal state proper.

Effect (a) will not cause any anisotropy, but (b) will cause differences ΔC among the Curie constants C for the different axes, of the order $\Delta C/C \sim q_b$. Hence, if (b) is really large enough to appreciably distort the magneton number, the coefficients of $1/T$ need not be exactly equal for the three axes as presupposed in (6), and anisotropy need not necessarily be reflected in deviations of individual susceptibilities from Curie's law. However, we doubt if (b) is usually large enough to be an important cause of anisotropy.

Quite irrespective of the low magnitude of q_a yielded by our rough numerical calculations, additional evidence that the effect (a) is not the cause of the observed deviations from the value 5.92 is furnished by the following consideration. It is very difficult to understand from (a) how the Curie constant could vary as much from salt to salt as observed experimentally. It is true that the effect (a) can depend somewhat on the nature of the salt, because the crystalline potential oftentimes may be comparable with the intervals separating the various states of d^5 , and so may modulate the frequencies ν_i differently in different manganous or ferric compounds. Nevertheless, one would expect some systematic variation characteristic of all salts if (a) is really important, whereas Jackson's values for five salts quoted above are about as often below as above 5.92. Effect (b) can vary markedly with the salt, but there is the difficulty on the order of magnitude. We are, therefore, inclined to believe that experimental error and crystalline imperfections are often the main cause of the discrepancy.

It is clearly to be understood that in other ions of the iron group which are not in S states the deviations of the Curie constants from the Bose-Stoner values are quite appreciable, and vary both with the crystalline axes and with the salt used. This is shown by the

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In the case of the rare earths the spin-orbit terms are larger than in the iron group. Hence, even if effect (a) is unimportant in Mn^{++} and Fe^{+++} , this correction for incipient $j-j$ coupling may cause the Curie constants to deviate appreciably (1 per cent. or so) from the Hund values in rare earths, whereas effect (b) is negligible. The deviation due to (a) should, however, vary but little with the salt, as the crystalline potential has a smaller value for the rare earth $4f$ orbits than the iron $3d$. It is thus exceedingly difficult to understand theoretically the large variations, over 5 per cent., which Selwood⁽¹⁸⁾ finds in the Curie constants of different neodymium salts.

3. THE PARAMAGNETIC ROTATION.

Saturation Effects in Spessartite.—The only manganous compounds for which Faraday data are available at very low temperatures are spessartite ($3MnO \cdot Al_2O_3 \cdot 3SiO_2$) and dialogite (principally $MnCO_3$)⁽¹⁹⁾. We shall consider first the former of these. At the temperature of liquid helium saturation effects enter. Such a temperature is presumably so low that only one pair of Stark levels is populated. This pair constitute a Kramers double level which is characteristic of atoms with an odd number of electrons and whose components cannot be separated by any crystalline field. Under such conditions, as Kramers has shown⁽²⁰⁾, one expects the rotation to depend on the field-strength in the fashion

$$\rho = \rho_\infty \tanh \mu \beta \mathbf{H} / kT, \quad \dots \quad (11)$$

where $\pm \mu \beta \mathbf{H}$ are the Zeeman energies of the two doublet components, and where ρ_∞ is the rotation at complete saturation. The constant μ is connected with the effective Bohr magneton number defined by (10) by the relation

$$n_B^2 = 3\mu^2. \quad \dots \quad (12)$$

Becquerel, de Haas, and van den Handel⁽¹⁹⁾ find that the saturation in spessartite can be represented fairly well if one takes $n_B^2 = 3$. This is disconcerting, for one can prove that for any Kramers doublet formed from the state $J=5/2$ the value of n_B^2 , averaged over the three

axes, cannot be less than $25g^2/12$. Since the Landé g -factor, has the value 2 in our case, the minimum possible value of n_B^2 is thus $25/3$. It is necessary to average over the three axes because spessartite has cubic symmetry. This does not demand that the local fields surrounding a given atom have cubic symmetry, but since this symmetry is possessed macroscopically, any departures from cubic type are averaged out when one considers a large number of atoms in a single crystal (21).

To prove that the minimum of n_B^2 is $25/3$, one proceeds as follows. The wave-functions Ψ_{\pm} appropriate to one of the components of the lowest Kramers doublet can be written as the sum of the wave-functions in the M system of representation. Only alternate values of M will be represented, so that

$$\Psi_{\pm} = p\psi_{\pm 5/2} + q\psi_{\pm 1/2} + (1-p^2-q^2)^{\frac{1}{2}}\psi_{\mp 3/2} \quad \dots \quad (13)$$

The two choices of sign yield the two components. The moments appropriate to (13) follow at once from the known elements of the magnetic moment in the M system of representation. We determine p and q to make the average of the squares of the moments along the x , y , and z axes a minimum. It is found that the minimum occurs at

$$p = -\left(\frac{1}{6}\right)^{\frac{1}{2}}, \quad q = 0, \quad \dots \quad \dots \quad \dots \quad (14)$$

and that the corresponding value of n_B^2 is $25g^2/12$. Now it can be shown that the choice (14) is precisely that which yields the linear combination appropriate to the irreducible representation Γ_7 of the cubic group contained in $J=5/2$. (The other cubic representation Γ_8 involved in $J=5/2$ is four-fold, and would yield much higher moments.) That the minimum should correspond to a cubic field is not at all surprising because of the high symmetry characteristic of cubes.

An escape from the contradiction between experiment and theory is provided if one assumes that the Heisenberg exchange effects are not negligible. It is well known that these effects are approximately equivalent to taking the effective local field as $\mathbf{H} + \alpha \mathbf{I}$, where α is a constant and \mathbf{I} is the intensity of magnetization. To act in the right direction for our purposes α must be negative, which is the sign found in most non-ferromagnetic

compounds⁽²²⁾, and which makes the exchange effect a demagnetizing one. Since I and ρ are surely proportional if only one Kramers doublet is inhabited, we can also write the effective field as $\mathbf{H} - a\rho$, where a is a positive constant. If one takes the argument of the hyperbolic tangent in (11) as $\mu(\mathbf{H} - a\rho)/kT$ rather than $\mu\mathbf{H}/kT$, one finds that with proper selection of a the experimental saturation data of Becquerel, de Haas, and van den Handel can be fitted with a much larger value of μ than previously, and fully as well. If we assume that μ^2 has its minimum theoretical value $25/9$, and if we take $\rho_\infty = 5.81$, $\Delta = 1.12$, then we obtain the theoretical saturation curve I, shown in fig. 1, which is seen to fit the experimental data adequately. No doubt equally satisfactory curves could be obtained with still higher pairs of values of μ and a , but in a material as magnetically dilute as spessartite it is probably best to avoid assuming the exchange effects any larger than necessary.

Temperature Variation in Spessartite.—At temperatures so low that only the lowest Kramers doublet is involved, the Verdet constant V (rotation per unit field strength per unit length⁽²³⁾) and the susceptibility χ should depend on the temperature in the fashion

$$\chi = \frac{I}{\mathbf{H}} = \frac{25N\beta^2}{9k(T + \Delta)}, \quad V = \frac{\rho}{\mathbf{H}} = \frac{(25/9)^{\frac{1}{2}}\rho_\infty\beta}{k(T + \Delta)}, \quad (15)$$

if we assume that $\mu^2 = 25/9$ and if we confine our attention, as we do henceforth, to fields too weak to give an appreciable saturation. The value of Δ is

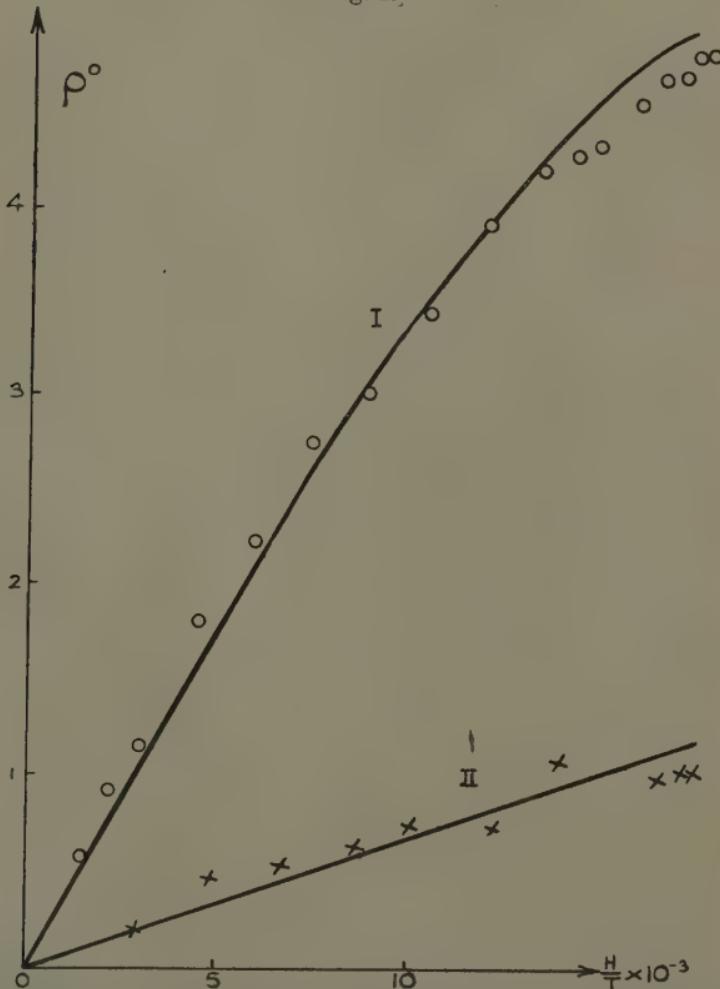
$$\Delta = (25/9)^{\frac{1}{2}}a\rho_\infty\beta/k, \quad \dots \quad (16)$$

and so $\Delta = 1.12$ if we use $a = 1720$, $\rho_\infty = 5.81$, as in drawing curve I in fig. 1. Formulae (15) and (16) are obtained from (11) by substituting $\mathbf{H} - a\rho$ for \mathbf{H} and replacing the hyperbolic tangent by its argument. The proportionality factor between χ and ρ is $\mu\beta/\rho_\infty$, because the values of I and ρ at complete saturation are respectively $\mu\beta$ and ρ_∞ . To preserve the relation (12) T must be replaced by $T + \Delta$ in the definition (10) of n_B ^{(23), (24)}.

When one turns to temperatures sufficiently high that other Stark components of $^6S_{5/2}$ have appreciable Boltzmann factors, one can no longer expect the Verdet constant and susceptibility to vary with temperature in the

same way. It is true that elsewhere M. H. Hebb and one of the writers will show that there is both theoretical and experimental evidence that in the rare earths, notably tysonite, the temperature dependence is the same for V and χ except for a constant of proportionality. One cannot, however, in general expect a similar simple

Fig. 1.



Curve I is a plot of $\rho = \rho_\infty \tanh \mu(\mathbf{H} - a\rho)/kT$, for the paramagnetic rotation ρ against \mathbf{H}/T for the crystal spessartite. The numerical values $\rho_\infty = 5.81$, $a = 1720$, $T = 1.475^\circ \text{K}$, were chosen to fit the experimental points of Becquerel, de Haas, and v. d. Handel, marked by circles, as well as possible with the minimum theoretical value $\mu = 5/3$. Curve II gives a similar plot for dialogite, but here the demagnetizing effect of exchange is very large, and any curve for which $a/\rho_\infty = 3800$ (a large) gives a straight line II.

correlation between V and χ in salts of the iron group, as such a correlation demands that the crystalline splitting of the ground state be small compared with its multiplet structure, whereas actually there is a virtually complete electric Paschen-Back effect in the iron group. In the particular case of ions normally in S states, special consideration is required because the ground state is devoid of multiplet structure. Here the existence of a non-vanishing paramagnetic rotation is due entirely to the fact that the different multiplet components of the important absorption lines have somewhat different frequencies. The proof of this proposition is furnished by study of Rosenfeld's⁽²⁵⁾ treatment of the Faraday effect of free atoms. He shows that without spin, S states are completely devoid of paramagnetic rotary power, and one can show that after addition of the spin the paramagnetic Faraday effect enters only in so far as the frequency denominators in the dispersion formula are different for the different components of a multiplet. Now the resonance lines of an ion having an S ground state are primarily of the form $S-P$, and so there is a multiplet structure for the upper levels of the transitions involved in absorption. Hence the frequency denominators can be different. The difference, is, however, not so large but that one should expect the paramagnetic rotation to be quite small, and of a different order of magnitude than in the case of ions whose ground states have $L > 0$. This offers an immediate explanation of Becquerel, de Haas, and van den Handel's observation that the Verdet constant is considerably smaller in spessartite than in rare earth salts such as tysonite.

The crystalline electric fields undoubtedly produce a tremendous Paschen-Back effect on the multiplet structure of the excited states. Consequently the small differences between the frequency denominators for the various multiplet components will be completely altered, in general, in the solid as compared with the free state. Thus the Verdet constant of 6S ions can be quite unlike in solids and in the idealized gas-phase, even at room-temperatures. On the other hand, the magnetic susceptibility is a property only of the ground level, and this will not be affected by the formation of solid compounds as long as the temperature is so high that the crystalline splitting of the ground state is small compared with kT .

We have seen in section 1 that this splitting is only an affair of a few wave-numbers, and so at ordinary temperatures solidification damages the paramagnetic rotation, but not the magnetic susceptibility. Hence in the solid state no simple proportionality between V and χ can in general be expected except at temperatures so low that (15) is applicable, although such a proportionality should be found for all temperatures were we capable of making measurements on free Mn^{++} .

There is, however, one case where a simple proportionality between V and χ , and hence a similar temperature variation for the two, may be expected. This is the case of a crystal in which the local crystalline fields have perfect cubic symmetry. Such a requirement is more stringent than that the crystal be of the cubic classification, as the cubic properties may be achieved macroscopically rather than microscopically (*e. g.*, the atoms might have three types of rhombic surroundings, differing only by cyclic interchange of axes; there is then macroscopic cubic symmetry if the three types are equally represented). The reason that a perfectly cubic field does not destroy the proportionality of V and χ is that such a field cannot produce a Stark splitting of P levels except when the interplay with spin-orbit terms is considered, since the orbital wave-functions appropriate to $L=1$ involve only the triply degenerate cubic representation ⁽³⁾ Γ_4 . This interplay was considered in section 1, and shown to give rise to splittings which are comparatively small. They may be somewhat larger in P states than our estimates for the splittings in S states, because the perturbation calculation need not be carried so far to exhibit the separation. In fact it appears probable that the cubic splitting of P states first enters in the approximation $[H_2]^2 H / h^2 \nu_1^2 \sim 10^{-1}$ cm. In any case this splitting is presumably small compared with the multiplet separation, *e. g.*, the individual Stark patterns of $^6P_{7/2}$, $^6P_{5/2}$, and $^6P_{3/2}$ are small compared with the free multiplet intervals $^6P_{7/2} - ^6P_{5/2}$, $^6P_{5/2} - ^6P_{3/2}$. Hence there need be no appreciable Paschen-Back effect on P levels in perfectly cubic fields. Since the resonance lines are of the form $^6S - ^6P$, both the ground and important excited states will be but slightly disturbed. Consequently the paramagnetic rotation will be substantially the same in the solid as in the gas state, unless

the temperature is reduced so low that the Stark components of the ground state possess essentially different Boltzmann factors. One can, however, easily see that this Boltzmann effect enters in precisely the same way as it does in the magnetic susceptibility. Hence in manganous or ferric salts in which the crystalline fields are perfectly cubic, V and χ should differ only by a proportionality factor which is independent of temperature.

Unfortunately one has no susceptibility data with which to try this point in spessartite. An indirect test is, however, furnished by the following procedure. If χ and V are always proportional, the Verdet constant at room-temperatures should have the value

$$V = 35\rho_\infty \beta (9/25)^{1/2} / 3kT. \quad \dots \quad (17)$$

This is true at such temperatures where the Boltzmann factors for all the components of $^6S_{5/2}$ are substantially equal and the demagnetizing correction is negligible, so that χ is given by (1) with $S=5/2$. The proportionality factor is determined from the formulæ (15), which apply at very low temperatures. The increase in the magneton number from the low value involved in (15) to the much higher value $(35)^{1/2}$ in (1) is, of course, because more Stark levels become inhabited as the temperature is raised.

Before (17) can be applied to experimental data it is necessary to segregate the paramagnetic and diamagnetic rotations, since (17) applies only to the paramagnetic portions. The sum of the two is, of course, what is observed experimentally. The diamagnetic part of the Verdet constant can be determined from the experimental measurements at 77.5° and 302° K., if one assumes that the paramagnetic contribution obeys the Curie formula C/T over the interval $77-302^\circ$. The diamagnetic term D is independent of temperature. Knowing the empirical values of $D+C/T$ for two different values of T , one can immediately calculate D . This procedure⁽²⁶⁾ gives a value -0.0000474 for the diamagnetic part of the Verdet constant. Knowing D , we can henceforth immediately "subtract out" the diamagnetic rotation so as to obtain the purely paramagnetic part. The diamagnetic correction is naturally of subordinate, though not negligible, importance at low temperatures, and has been made before drawing

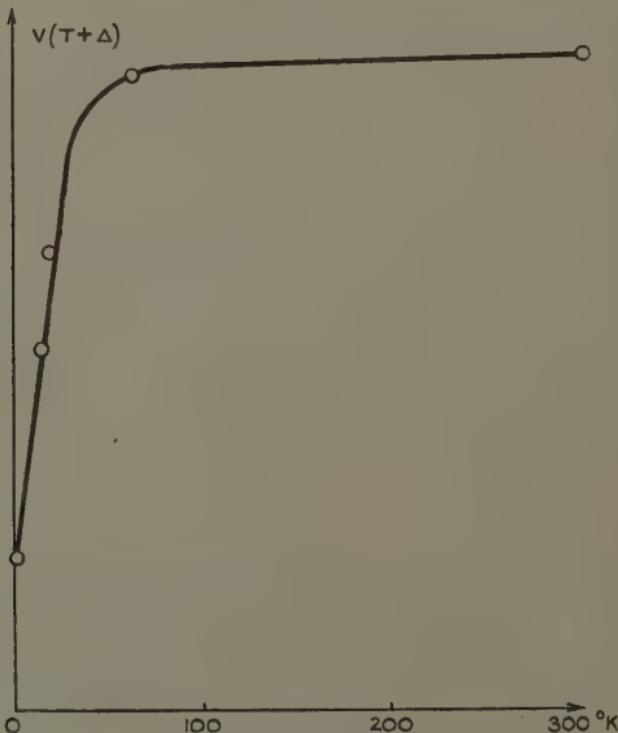
fig. 1. At room-temperatures the diamagnetic term is over five times greater than the paramagnetic. This overshadowing of the paramagnetic rotation by the diamagnetic is additional evidence that the former is a comparatively small effect in S states, as predicted by theory.

After making the diamagnetic correction, we find that the rotation observed at 302° K. demands a factor 35 in (17), just as it did for the low-temperature observations, provided we take the same value of $\rho_\infty = -5.81$. That it is possible to get exact agreement is because the rather scattered nature of the experimental points at helium-temperatures allows us a little latitude in the choice of a and ρ_∞ , the corresponding values of the above factor ranging around 35. As we have explained already, there is no need for this numerical factor to be exactly the same at helium- and room-temperatures unless the crystalline field has microscopic cubic symmetry. Nevertheless, it is gratifying that the experimental results should show that they must be taken, at any rate, nearly equal, especially when it is remembered that the observed paramagnetic rotation deduced from the slope of the $\rho - \mathbf{H}$ curve at the origin varies by a factor 30 : 1, and the square of the magneton number has changed in the ratio 8½ : 35.

Eqs. (15) and (17) are respectively valid only if the Stark splitting of 6S is either very large or very small compared with kT . At intermediate temperatures—for instance, those of hydrogen—the rotation can be calculated from the general theory of the temperature variation of magnetic susceptibilities, provided we assume that V and χ are proportional. In these calculations it is assumed that the crystalline field has cubic symmetry, so that the upper Stark component of 6S is four-fold. We shall not give the formulæ appropriate to intermediate temperatures, since they are more complicated than (15) or (17), and since the assumption of proportionality between χ and V is questionable in spessartite. It is found that then the temperature variation of the rotation, after subtraction of the diamagnetic portion, can be fitted reasonably well, as shown in fig. 2, if we assume that the crystalline splitting is 27 cm.^{-1} . So large a separation seems improbable in view of our estimates of the order of magnitude in section 1, as well

as the observed behaviour of manganese ammonium sulphate studied in section 2. It is true that the separations of 6S Stark components may vary more from crystal to crystal than in the usual case $L>0$, because the constants of the crystalline field are often raised to powers above the first in our expressions for $\hbar\Delta\nu$ in section 1. Nevertheless, it is rather hard to

Fig. 2.



The curve shows $V(T + \Delta)$ against T , where V is the paramagnetic part of the Verdet constant obtained directly from the experimental results and $\Delta = 1.12^\circ$, this latter being chosen to make the "slope" and "curvature" values of μ at helium-temperatures equal to the minimum value $5/3$. If we assume that V and χ are proportional, and that at 302° K. the square of the magneton number has the "spin-only" value 35, we can fit the $n_B^2 - T$ curve so obtained by the field of cubic symmetry which produces a splitting of the $^6S_{5/2}$ state of 27 cm^{-1} .

believe that the splitting could be only about 1 cm^{-1} in $\text{MnSO}_4(\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ and 27 cm^{-1} in $3\text{MnOAl}_2\text{O}_3 \cdot 3\text{SiO}_2$.

We are, therefore, forced to conclude that our attempts to establish proportionality between V and χ in spessartite are probably spurious except at very low temperatures. We have given our theoretical discussion not so much because it might be applicable to spessartite as in the hope it may encourage future experimental measurements on the temperature variation of both the susceptibility and Faraday effect of manganous or ferric salts which are free from impurities and in which the surroundings of the ions have microscopic cubic symmetry. The application to spessartite is questionable for various reasons : (a) the results at high temperatures are rather sensitive to the large diamagnetic correction ; (b) iron is contained in spessartite as an impurity ; (c) the surroundings of the Mn^{++} ion are not accurately cubic. The difficulty (a) would, of course, be unavoidable even if other manganous compounds are used ; we are inclined to believe that in spessartite (a) is less likely the trouble than (b) or (c). It is known that iron is present in the ratio of one iron atom to about sixteen of manganese in the particular crystal used by Becquerel, de Haas, and van den Handel. If the iron is exclusively in the ferric form, the resulting error is not serious. However, if any of the iron is in the ferrous condition, the rotation per iron ion is enormously greater than that per manganese, since the former has $L > O$. Hence a small amount of iron impurity may distort the Faraday rotation enormously, even though it does not the susceptibility. As regards (c), it is known from X-ray data that the eight oxygen atoms surrounding a given Mn^{++} ion are approximately equidistant from the latter, and are arranged in such a way that two rhombic disphenoids can be constructed on them as lattice-points⁽²⁸⁾. In other words, the O atoms lie very near to the corners of a cube. The microscopic field acting on the Mn^{++} ions, therefore, does not depart much from cubic symmetry. Even if the source of error (c) is important for the temperature dependence, it still does not enter into our discussion of saturation effects at low temperatures, whereas (b) does.

Dialogite.—The constitution of this mineral is mainly $MnCO_3$, and hence the exchange effects may be large. This is reflected in the fact that the rotation per Mn

ion is much smaller in dialogite than in spessartite, as can be seen by comparing the two graphs in fig. 1. It is, however, conceivable that the greater rotation in spessartite is due to a ferrous impurity. The iron contamination in dialogite is known to be very small. If we use (15), and if we assume that, allowing for the different density of Mn atoms, the constant ρ_∞ has the same value in dialogite as in spessartite, then the Verdet constant observed for the former demands $\Delta=11^\circ$. Only the order of magnitude should be considered reliable, since the diamagnetic correction in spessartite is uncertain. Also there is no reason why ρ_∞ should be the same, for dialogite belongs to the rhombohedral system, and so the distortion effects on the frequency denominators in $^6S-^6P$ transitions may be very large. Nevertheless, this different order of magnitude for ρ_∞ in dialogite than in spessartite is qualitative evidence for much greater exchange effects in the former. According to Sucksmith⁽²⁹⁾, the susceptibility of $MnCO_3$ at room-temperatures is about 25 per cent. below the "spin only" value (1). This demands a Δ of the order 100° if the anomaly is attributed to exchange demagnetization. Only qualitative comparisons with Sucksmith's data are probably allowable, as he used an artificial manganese carbonate rather than the mineral. Regardless of whether Δ is 11° or 100° , the exchange demagnetization effects are so large that it should be almost impossible to observe saturation curvature in dialogite even at the temperature of liquid helium. Becquerel, de Haas, and van den Handel claim to have deduced an effective magneton number approximately $3\frac{1}{2}$ from the curvature. However, the experimental points are very scattered, and it is seen from fig. 1 that their general drift can be fitted reasonably well by a straight line.

SUMMARY.

Formulæ are developed for the temperature variation and anisotropy in the susceptibility of manganous or ferric compounds of high magnetic dilution. The Faraday effect in these particular materials is also discussed. It is shown that if the crystalline field has perfect cubic symmetry there are theoretical grounds for believing the susceptibility and paramagnetic part of the Verdet

constant to be proportional. In this special case, therefore, these two quantities should exhibit the same temperature dependence. The comparison with experiment can be made only qualitatively, and hence is rather disappointing, because of the dearth and contradictory nature of the existing experimental data. It is hoped that the present discussion may stimulate new measurements on both susceptibility and rotation. We have also tried to make clear the need for great caution in attempts to deduce magneton numbers from Faraday curvatures in manganous compounds, because of potentially large exchange demagnetizing effects and possible ferrous impurities. Such impurities, unless large in amount or ferromagnetic in nature, will not damage susceptibility in distinction from rotation data.

REFERENCES.

- (1) E. C. Stoner, Phil. Mag. viii. p. 250 (1929); H. Bethe, *Ann. der Physik*, iii. p. 133 (1929); H. A. Kramers, Proc. Amsterdam Acad. xxxii. p. 1176 (1929); J. H. Van Vleck, 'The Theory of Electric and Magnetic Susceptibilities,' Chap. xi.; W. G. Penney and R. Schlapp, Phys. Rev. xli. p. 194 (1932); R. Schlapp and W. G. Penney, *ibid.* xlvi. p. 666 (1932).
- (2) I. I. Rabi, Phys. Rev. xxix. p. 184 (1927).
- (3) H. Bethe, *Ann. der Physik*, iii. p. 133 (1929).
- (4) H. A. Kramers, Proc. Amsterdam Acad. xxxiii. p. 959 (1930).
- (5) S. Goudsmit, Phys. Rev. xxxi. p. 946 (1928).
- (6) It is to be clearly understood that in the present paper we are concerned only with salts wherein the susceptibility has at room-temperatures approximately the value which one calculates on the assumption that the Mn^{++} or Fe^{+++} ion has a spin-quantum number $S=5/2$. This will be the case if one can utilize, even in the solid compound, the Hund rule that 6S is the deepest state of d^5 . There are, however, known to be manganous and ferric compounds, notably the cyanide complex salts such as $K_3Fe(CN)_5$, whose susceptibility is given approximately by (1), provided one takes $S=\frac{1}{2}$ rather than $S=5/2$. As will be discussed more fully elsewhere, this anomaly is simply explained if we assume that in the cyanides, etc., the crystalline potential is large compared with the separation between the different multiplets arising from d^5 . There is, then, an electric Paschen-Back effect even on the compounding of the l 's to a resultant L , and one can no longer use the Hund rule that the ground state has the maximum possible spin. Another explanation of the anomaly has been given by Pauling, but with a very specialized mechanism (J. Amer. Chem. Soc. lxxi. p. 1367, 1931). In the sulphates the crystalline field is not large enough to break down the L -coupling, but still can modify the intervals between the different multiplets.
- (7) For discussion of the procedure when the degeneracy is removed only in the higher approximations, see, for instance, J. H. Van Vleck, Phys. Rev. xxxiii. p. 467 (1929), or Born and Jordan, 'Elementare Quantenmechanik,' pp. 209, ff. Also see especially

Penney and Schlapp, *Phys. Rev.* xli. p. 194 (1932), for further elucidation on the relation of the crystalline potential to the structure of the secular determinant.

(8) C. J. Gorter, *Arch. Musée Teyler*, vii. (3), p. 183 (1932); or R. Schlapp and W. G. Penney, *Phys. Rev.* xlvi. p. 670 (1932).

(9) W. G. Penney and R. Schlapp, *Phys. Rev.* xli. p. 198 (1932); also the preceding reference.

(10) See especially the measurements of Jackson and Onnes on powdered manganese ammonium sulphate and of Onnes and Oosterhuis on ferric alum at low temperatures (Leiden Comm. 168 b, 139 e). For these materials Curie's law holds for the powder right down to hydrogen temperatures within the experimental error.

(11) Jackson and de Haas, *Leiden Comm.* 187.

(12) L. C. Jackson, *Proc. Roy. Soc. exl.* p. 695 (1933).

(13) K. S. Krishnan, N. C. Chakravorty, and S. Banerjee, *Phil. Trans. Roy. Soc. cxxxii.* p. 99 (1933).

(14) K. S. Krishnan, *Zeits. f. Physik*, lxxi. p. 137 (1931).

(15) H. Kamerlingh Onnes and E. Oosterhuis, *Leiden Comm.* 132 e.

(16) For the experimental data, see Onnes and Oosterhuis, *Leiden Comm.* 129 b, 132 e.

(17) Onnes and Oosterhuis state that their manganese chloride was not completely anhydrous, and so one naturally wonders whether the water present might separate the Mn ions sufficiently to largely suppress the exchange effect, and thus explain the absence of an appreciable Δ for $MnCl_2$ in (9). It is very doubtful whether there was enough water for this. Also Mr. R. B. Janes has made new measurements on $MnCl_2$ at Wisconsin, and reports a close conformity to Curie's law down to liquid-air temperatures (the lowest investigated in his experiments), even when the dehydration is quite complete.

(18) P. W. Selwood, *J. Amer. Chem. Soc.* lv. p. 3161 (1933).

(19) Jean Beequerel, W. J. de Haas, and J. van den Handel, *Leiden Comm.* 218; or *Proc. Amsterdam Acad.* xxxiv. p. 1231 (1931).

(20) H. A. Kramers, *Proc. Amsterdam Acad.* xxxii. p. 1176 (1929); xxxiii. p. 959 (1930); H. A. Kramers and J. Beequerel, *ibid.* xxxii. p. 1190 (1929).

(21) When the cubic symmetry is macroscopic rather than microscopic, eq. (11) is not strictly applicable. Instead, it should be averaged over the three axes. Then the apparent value of n_B deduced from the saturation curvature by attempted use of (11-12) without averaging is always *greater* than the more fundamental n_B deduced from theory or susceptibility measurements in weak fields by means of (10). This will be shown elsewhere by M. H. Hebb and the writer. Hence in no case should application of (11-12) to the experimental data yield a lower value of n_B^2 than $25/3$. The distinction between the apparent and true values of n_B (not to be confused with the two modes of definitions of n_B to be discussed in note 24) need not worry us, since in fig. 1, etc., we base our calculations on $\mu^2=25/9$, and this demands the full microscopic cubic symmetry.

(22) Cf., for instance, J. H. Van Vleck, 'The Theory of Electric and Magnetic Susceptibilities,' pp. 348-349.

(23) The unit of length is taken to be 1 mm., as in Beequerel's work, whenever we quote numerical figures. The values of ρ , which we give likewise, are reduced to a path of 1 mm., so that length does not enter as a proportionality factor between ρ and V .

(24) Whether or not this modification in (10) is made when exchange effects are present is, of course, purely a matter of convention. In Van Vleck's book the Δ term is never introduced in the

definition of the effective magneton number in terms of the susceptibility, because in general one can never tell how much of the departure from Curie's law is due to crystalline fields and how much to exchange. Only with the modified form of (10) can we, of course, conclude that the minimum value of n_B^2 is $25/3$, etc.

(25) L. Rosefeld, *Zeit. f. Phys.* lvii. p. 835 (1929).
(26) Due to an arithmetical error, Becquerel, de Haas, and van den Handel give 0000465 for the diamagnetic part of V as obtained by this method.
(27) Had μ in (11) etc. been taken larger than its minimum value $(25/9)\frac{1}{2}$, and the exchange demagnetizing field correspondingly larger, so as to still give the proper amount of saturation curvature at helium-temperatures, one would find that the experimental value of V at room-temperatures would require a factor much larger than 35. This is an argument for taking μ equal to its minimum value, but cannot be regarded as conclusive, since we shall shortly see that the use of (17) in spessartite is questionable.
(28) P. P. Ewald and C. Hermann, 'Strukturbericht,' pp. 366 & 411.
(29) W. Sucksmith, *Proc. Roy. Soc. A*, cxxxiii. p. 169 (1931).

LXXIX. *On the Solution of Boundary Problems in Mathematical Physics.* By JACOB NEUFELD, Moore School of Electrical Engineering, University of Pennsylvania, U.S.A.*

IN one of the recent articles of Dr. B. van der Pol⁽¹⁾ is shown a method of solving a differential equation of order n in the case in which the unknown function $y(t)$ and its derivatives up to the order $n-1$ are given at the initial instant. The method of Dr. van der Pol consists in multiplying each term of the differential equation by $e^{-pt} dt$ and integrating the result from zero to infinity. The procedure consists in finding first the "image" $f(p)$ of the unknown function, which is defined by the Laplacian integral

$$\frac{f(p)}{p} = \int_0^\infty e^{-pt} y(t) dt, \dots \dots \dots \quad (1)$$

and subsequently determining the function y by applying any of the processes developed by Oliver Heaviside⁽²⁾.

The present note contains a similar method of attack, and an attempt is made to solve the Dirichlet's or Neumann's problem in partial differential equations of

* Communicated by the Author.

the elliptic type. In order to illustrate the procedure a simple example is taken.

Consider the equation

$$\frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} = \alpha^2 H, \dots \dots \quad (2)$$

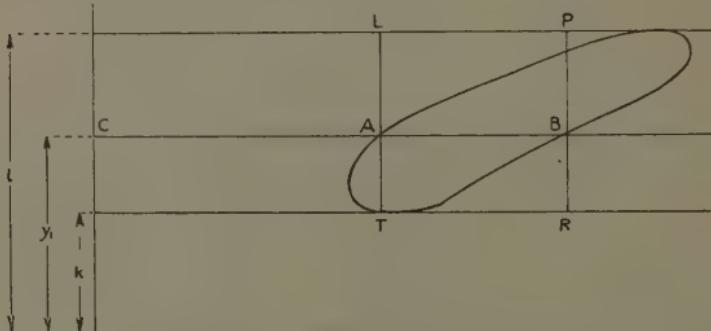
and let the function $H(xy)$ assume the value S along the boundary of the curve shown in the figure. Let $y=y_1$ be a line cutting the boundary curve in two points A and B , and let

$$CA = \phi_1(y_1),$$

$$CB = \phi_2(y_1)$$

for any value

$$k \leq y \leq l.$$



Consider a rectangle $TLPR$ formed by the sides

$$TL = PR = l - k \quad \text{and} \quad TR = LP = \phi_2(y_1) - \phi_1(y_1).$$

We can express the function $H(xy)$ for any point within the rectangle in form of a double Fourier's series :

$$H(xy) = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} C_{mn} e^{i(mx+ny)}, \dots \dots \quad (3)$$

where

$$C_{mn} = \frac{1}{(l-k)[\phi_2(y_1) - \phi_1(y_1)]} \int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} H(xy) e^{-i(mx+ny)} dx dy. \dots \dots \quad (4)$$

The present method consists of finding the Fourier's constants C_{mn} , which, when substituted in the expression (3), will give the value of the unknown function for any

point within the rectangle TLPR. Since y_1 may vary from k to l , the expression (3) can give the solution for any point within the given boundary.

Let us multiply both sides of the equation (2) by $\epsilon^{-i(mx+ny)} dx dy$, and let us integrate the obtained result with respect to x from $\phi_1(y_1)$ to $\phi_2(y_1)$ and with respect to y from k to l .

We obtain then

$$\int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} \frac{\partial^2 H}{\partial x^2} \epsilon^{-i(mx+ny)} dx dy + \int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} \frac{\partial^2 H}{\partial y^2} \epsilon^{-i(mx+ny)} dx dy \\ = a^2 \int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} H \epsilon^{-i(mx+ny)} dx dy. \dots (5)$$

By applying successive integrations, the first term of the left-hand side of this equation can be transformed in the following way:

$$\int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} \frac{\partial^2 H}{\partial x^2} \epsilon^{-i(mx+ny)} dx dy = \int_k^l \epsilon^{-iny} \left[\frac{\partial H}{\partial y} \right]_{x=\phi_1(y_1)}^{x=\phi_2(y)} dy \\ + im \int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} \frac{\partial H}{\partial x} \epsilon^{-i(mx+ny)} dx dy \\ = \int_k^l \epsilon^{-iny} \left[\frac{\partial H}{\partial x} \epsilon^{-imx} \right]_{x=\phi_1(y_1)}^{x=\phi_2(y_1)} dy + im \int_k^l \epsilon^{-iny} \left[H \epsilon^{-imx} \right]_{x=\phi_1(y_1)}^{x=\phi_2(y_1)} dx \\ - m^2 \int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} H \epsilon^{-i(mx+ny)} dx dy. \dots (6)$$

Due to the relation

$$[H]_{x=\phi_1(y_1)} = [H]_{x=\phi_2(y_1)} = S, \dots \dots \dots (7)$$

and to the relation (4), the expression (7) becomes

$$\int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} \frac{\partial^2 H}{\partial x^2} \epsilon^{-i(mx+ny)} dx dy = \int_k^l \epsilon^{-iny} \left[\frac{\partial H}{\partial x} \epsilon^{-imx} \right]_{x=\phi_1(y_1)}^{x=\phi_2(y)} dy \\ - \frac{m}{n} S [\epsilon^{-im\phi_2(y_1)} - \epsilon^{-im\phi_1(y_1)}] [\epsilon^{-inl} - \epsilon^{ink}] - m^2(l-k)[\phi_2(y_1) \\ - \phi_1(y_1)] C_{mn}. \dots (8)$$

In a similar way

$$\int_k^l \int_{\phi_1(y_1)}^{\phi_2(y_1)} \frac{\partial^2 H}{\partial y^2} \epsilon^{-i(mx+ny)} dx dy = \int_{\phi_1(y_1)}^{\phi_2(y_1)} \epsilon^{-imx} \left[\frac{\partial H}{\partial y} \epsilon^{-iny} \right]_{y=k}^{y=l} dx - \frac{n}{m} S [\epsilon^{-im\phi_2(y_1)} - \epsilon^{-im\phi_1(y_1)}] [\epsilon^{-inl} - \epsilon^{-ink}] - n^2(l-k)[\phi_2(y_1) - \phi_1(y_1)] C_{mn}. \quad (9)$$

On account of the relations (4), (8), and (9), the expression (5) becomes

$$\int_k^l \epsilon^{-iny} \left[\frac{\partial H}{\partial x} \epsilon^{-imx} \right]_{x=\phi_1(y_1)}^{x=\phi_2(y_1)} dy + \int_{\phi_1(y_1)}^{\phi_2(y_1)} \epsilon^{-imx} \left[\frac{\partial H}{\partial y} \epsilon^{-iny} \right]_{y=k}^{y=l} dx - S [\epsilon^{-im\phi_2(y_1)} - \epsilon^{-im\phi_1(y_1)}] [\epsilon^{-inl} - \epsilon^{-ink}] \left[\frac{m}{n} + \frac{n}{m} \right] = (m^2 + n^2 - \alpha^2)(l-k)[\phi_2(y_1) - \phi_1(y_1)] C_{mn}. \quad (10)$$

Let

$$\int_k^l \epsilon^{-iny} \left[\frac{\partial H}{\partial x} \epsilon^{-imx} \right]_{x=\phi_1(y_1)}^{x=\phi_2(y_1)} dy + \int_{\phi_1(y_1)}^{\phi_2(y_1)} \epsilon^{-imx} \left[\frac{\partial H}{\partial y} \epsilon^{-iny} \right]_{y=k}^{y=l} dx = R_{mn}. \quad (11)$$

Then

$$C_{mn} = \frac{-S(\epsilon^{-im\phi_2(y_1)} - \epsilon^{-im\phi_1(y_1)})(\epsilon^{-inl} - \epsilon^{-ink}) \left(\frac{m}{n} + \frac{n}{m} \right) + R_{mn}}{(m^2 + n^2 - \alpha^2)(l-k)[\phi_2(y_1) - \phi_1(y_1)]}. \quad (12)$$

The expression R_{mn} can be determined in the following two ways:—

1. From equation (3) we have

$$\frac{\partial H}{\partial x} = \sum_{m_1=-\infty}^{\infty} \sum_{n_1=-\infty}^{\infty} i m_1 C_{m_1 n_1} e^{i(m_1 x + n_1 y)}$$

and

$$\left[\frac{\partial H}{\partial x} \epsilon^{-imx} \right]_{x=\phi_1(y_1)}^{x=\phi_2(y_1)} = \sum_{m_1=-\infty}^{\infty} \sum_{n_1=-\infty}^{\infty} i m_1 C_{m_1 n_1} e^{i n_1 y} [\epsilon^{i(m_1 - m)\phi_2(y_1)} - \epsilon^{i(m_1 - m)\phi_1(y_1)}]. \quad (13)$$

Similarly,

$$\left[\frac{\partial H}{\partial y} e^{iny} \right]_{y=k}^{y=l} = \sum_{m_1=-\infty}^{\infty} \sum_{n_1=-\infty}^{\infty} i n_1 C_{m_1 n_1} e^{im_1 x} [e^{i(n_1-n)l} - e^{i(n_1-n)k}]. \quad \dots \quad (14)$$

Substituting (13) and (14) in (11), we obtain

$$\begin{aligned} R_{mn} &= \sum_{m_1=-\infty}^{\infty} \sum_{n_1=-\infty}^{\infty} \frac{m_1}{n_1-n} C_{m_1 n_1} [e^{i(m_1-m)\phi_2(y_1)} - e^{i(m_1-m)\phi_1(y_1)}] \\ &\quad \times [e^{i(n_1-n)l} - e^{i(n_1-n)k}] \\ &\quad + \frac{n_1}{m_1-m} C_{m_1 n_1} [e^{i(n_1-n)l} - e^{i(n_1-n)k}] \\ &\quad \times [e^{i(m_1-m)\phi_2(y_1)} - e^{i(m_1-m)\phi_1(y_1)}] \\ &= \sum_{m_1=-\infty}^{\infty} \sum_{n_1=-\infty}^{\infty} C_{m_1 n_1} \left[\frac{m_1}{n_1-n} + \frac{n_1}{m_1-m} \right] \\ &\quad \times [e^{i(m_1-m)\phi_2(y_1)} - e^{i(m_1-m)\phi_1(y_1)}] [e^{i(n_1-n)l} - e^{i(n_1-n)k}]. \quad \dots \quad (15) \end{aligned}$$

The expression (15) can be computed by successive substitutions. We assume at first that R_{mn} entering in the expression (11) is zero, and we substitute the obtained value for C_{mn} in (15). We obtain then a value for R_{mn} which, substituted in (14), gives the next value for C_{mn} , which, substituted again in (15), gives the next value for R_{mn} , and so on.

As often occurs in Operational Calculus, also in this case, we deal with an infinite process in which the convergence of the result needs to be established in each specific problem.

2. The value R_{mn} can also be computed in various cases in a different manner.

Consider, for instance, our equation $\nabla^2 H = \alpha^2 H$ under its given boundary conditions, but assume that α is very great. This occurs, for instance, in study of the penetration of a high-frequency electromagnetic field into a cylindrical conductor of a given shape. Henri Poincaré⁽³⁾ has given the following method for approximate determination of the value of the normal derivative in any point of the boundary in this particular problem:—

It is known that the function $H(xy)$ cannot attain its maximum inside the boundary, and consequently it

assumes the greatest values on the boundary. Take a new axis of coordinates by placing the origin on any point of the boundary, the x' -axis along the tangent, and the y' -axis along the normal to the boundary line. We have then

$$\frac{\partial^2 H}{\partial y'^2} + \frac{\partial^2 H}{\partial x'^2} = \alpha^2 H.$$

We have assumed that the value of the function is constant along the boundary, and, therefore, for every point approaching the origin as close as possible, $\frac{\partial H}{\partial x'}$ tends to zero, and our equation becomes

$$\frac{\partial^2 H}{\partial y'^2} = \alpha^2 H.$$

Then

$$H = A e^{ay'} - B e^{-ay'}.$$

Let, for instance, α be a complex number, in which the real part is negative. Since we have assumed that α is very great, as occurs when the electromagnetic field under consideration is of a very high frequency, the term $B e^{-ay'}$ increases very rapidly with y' , and H may become greater than its value on the boundary. This, however, is not possible, and, therefore, the term B must be very small compared with A . Consequently we can assume that

$$H = S e^{ay'},$$

and that in any point of the boundary the value of the normal derivative is

$$\frac{\partial H}{\partial n} = \alpha S.$$

This value, substituted in (11), gives R_{mn} with sufficient approximation in many practical problems.

In conclusion the author wishes to express his thanks to Professor J. G. Brainerd for his interest in the present work.

References.

- (1) B. van der Pol, "A Simple Proof and an Extension of Heaviside's Operational Calculus for Invariable Systems," *Phil. Mag.* vii. p. 1153 (1929).
- (2) See, for instance, J. R. Carson, 'Electric Circuit Theory and the Operational Calculus,' McGraw-Hill Book Co., Inc., New York, 1926.
- (3) H. Poincaré, "Etude du Récepteur Téléphonique," *L'Eclairage Electrique*, l. p. 335 (1907).

LXXX. *The Wave-statistical Theory of Electron Spin.*
*By K. C. KAR and K. K. MUKHERJEE**

THE quantum mechanical theories of electron spin have been given by Dirac †, Darwin ‡, Pauli §, Heisenberg-Jordan ||, and also Hartree ¶. Pauli's theory is simple but does not appear to be very rigorous in so far as he freely uses the vector rule for l, s, j . Darwin's theory, especially his later modification **, appears to us to be essentially the same as that of Dirac. Both have used the idea of non-commutative association of certain coefficients somewhat arbitrarily introduced, in order to ensure the splitting of the second-order wave equation of Schrödinger. Now the object of all these theories is primarily to get the correct Sommerfeld formula without the $\frac{1}{2}$ -quantum numbers which are obtained from the direct wave-statistical method.

In a recent paper †† we have shown that Dirac's result may be obtained without introducing the non-commutative principle, if we start with two second-order R-equations, instead of the usual one, with the values of l differing by unity. Even then the process of breaking up of the second-order equations into linear equations by the usual method and the idea of non-commutative association inherent in the nature of such a process could not be avoided. Moreover, in the above paper we could not explain the possible physical significance of taking two R-equations with different l .

In the present paper ‡‡ we shall show that one is justified in taking two R-equations as above, and that any one of them may yield the correct eigenvalue of energy. Thus to get the Sommerfeld-Dirac formula it is not at all necessary to split the R-equations.

* Communicated by the Authors.

† Dirac, Proc. Roy. Soc. A, cxvii. p. 610, 1928 *et seq.*

‡ Darwin, Proc. Roy. Soc. A, cxvi. p. 227, 1927 *et seq.*

§ Pauli, *Zeit. f. Phys.* xxxvi. p. 336 (1926); he gives later on a rigorous treatment with matrix-operators, *vide Zeit. f. Phys.* xlivi. p. 601 (1927).

|| W. Heisenberg and P. Jordan, *Zeit. f. Phys.* xxxvii. p. 263 (1926).

¶ Hartree, Proc. Camb. Soc. xxiv. p. 89 (1928).

** Darwin, Proc. Roy. Soc. cxviii. p. 654 (1928).

†† Kar and Mukherjee, Ind. Phys. Math. Journ. iii. p. 65 (1932); see also 'Science Abstracts,' p. 1233 (1932).

‡‡ The result has been announced in 'Current Science,' p. 309, April 1933.

The well-known χ_1 or χ_2 equations are

$$\Delta\chi + \frac{8\pi^2m}{h^2} (E - V)\chi = 0, \text{ non-relativistic. . . . (1)}$$

$$\Delta\chi + \frac{4\pi^2}{h^2c^2} [(E - V)^2 - E_0^2]\chi = 0, \quad E_0 = m_0c^2, \\ \text{relativistic. . . (2)}$$

Taking the solution in the usual form

$$\chi = RP_l^m(\cos\theta)e^{im\phi}, \quad (3)$$

we have for the R-equation

$$\frac{d^2R}{dr^2} + \frac{2}{r} \cdot \frac{dR}{dr} + \left(A + 2\frac{B}{r} + \frac{C}{r^2} \right) R = 0, \quad . . . (4)$$

where, in case of ordinary Kepler problem,

$$A = \frac{8\pi^2m}{h^2} E, \quad B = \frac{4\pi^2m}{h^2} \cdot Ze^2, \quad C = -l(l+1), \quad . . (5)$$

and in the case of relativistic orbit

$$A = \frac{4\pi^2}{h^2c^2} (E^2 - E_0^2), \quad B = \frac{4\pi^2}{h^2c^2} \cdot Ze^2E, \\ C = -l(l+1) + \frac{4\pi^2Z^2e^4}{h^2c^2}. \quad . . . (6)$$

In the above theory, well-known in wave-statistics, the effect of the spin of the electron is completely ignored. If we take this into account, remembering that to the first order the spin energy is negligible compared with the orbital energy of the electron, we find that the arguments leading to equation (5) cannot be materially changed. But in the relativistic case the small correction added to C is to be further corrected for spin, as we shall see presently.

Now, we know that the spin moment is $\pm \frac{1}{2}$ according as it is in the same or in the opposite sense with respect to the orbit. Therefore the total moment is $l + \frac{1}{2}$ or $l - \frac{1}{2}$, as the case may be. It is well known in quantum theory that in the former case l has the minimum value 0, whereas in the latter it is 1. The dynamical basis of this difference in the minimum values may be seen without difficulty when it is remembered that the orbital moment should always decide the sign of the resultant moment. Now we know that in (5)

$l_{\min.} = 0$. Therefore the R-equation (4) with C given in (5) cannot be used for the negative spin. In this case C should be

$$C = -(l-1)l, \dots \quad (7)$$

giving a second R-equation for the negative spin only. It is evident that the eigenvalues of energy in the two cases are given by

$$\left. \begin{aligned} \frac{B}{\sqrt{-A}} &= n_r + l + 1, & +\text{spin}, \\ \frac{B}{\sqrt{-A}} &= n_r + l, & -\text{spin}, \end{aligned} \right\} \dots \quad (8)$$

and they are the same on account of the difference in $l_{\min.}$. Thus to a first order there is no difference in energy.

Relativistic Kepler Problem.—The relativistic velocities of χ_1 and χ_2 waves as usually determined do not take into account the spin of the electron. Thomas has recently shown that in the case of spinning electron moving in an orbit one should use Lorentz transformation for a rotating axis. With this idea he finds that the total relativity effect is to produce the usual change of mass, and in addition, a precession at the rate

$$\omega = -\frac{Ze^2}{2m_0^2 c^2 r^3} \cdot \mathbf{L}, \dots \quad (9)$$

where c is the velocity of light, \mathbf{L} the angular momentum in the orbit being equal to $\frac{m_0}{\sqrt{1-\beta^2}} [\mathbf{r}\mathbf{v}]$, \mathbf{v} , velocity in the orbit, and the other symbols have their ordinary meaning. This precession is now known as the Thomas effect*. The energy corresponding to this well-known precession may easily be seen to be †

$$E_{\text{spin}} = (\omega \cdot s) = -\frac{Ze^2}{2m_0^2 c^2 r^3} \cdot (\mathbf{L} \cdot \mathbf{s}), \dots \quad (10)$$

where $s = \frac{\hbar}{4\pi}$, the angular momentum of the spin of the electron.

* L. H. Thomas, 'Nature,' cxvii, p. 514 (1926); Phil. Mag. iii, p. 1 (1927).

† Birtwistle, 'New Quantum Mechanics,' Cambridge, Art. 7.

Or we have

$$E_s = -\frac{Z^2 e^4}{4m_0 c^2 r^2 k \sqrt{1-\beta^2}} \quad \dots \quad (11)$$

We may point out that k in the above formula is the angular momentum. It has the minimum value 1. Therefore in the notation of wave-statistics it should be replaced by $l+1 (l=0, 1, \dots)$ for the positive spin and $l (l=1, 2, \dots)$ for negative spin. Thus (11) becomes in the new notation, putting $V = \frac{Ze^2}{r}$,

$$\left. \begin{aligned} E_s &= -\frac{V^2}{4E_0(l+1)\sqrt{1-\beta^2}}, & +\text{spin}, \\ &= -\frac{V^2}{4E_0 l \sqrt{1-\beta^2}}, & -\text{spin}. \end{aligned} \right\} \quad \dots \quad (12)$$

It is well known in the theory of relativity that

$$E_{\text{kin.}} = \frac{E_0}{\sqrt{1-\beta^2}}. \quad \dots \quad (13)$$

Now, putting for $E_{\text{kin.}}$ the total kinetic energy, namely, $(E-V)+E_s$, we get from (13)

$$E-V = \frac{E_0}{\sqrt{1-\beta^2}} \left(1 + \frac{V^2}{4k^2 E_0^2} \right) = \frac{E_0}{\sqrt{1-\beta^2}} \left(1 + \frac{V^2}{2k E_0^2} \right)^{\frac{1}{2}}. \quad (14)$$

neglecting higher terms. Hence from (14) on squaring and transforming, and finally after taking square root,

$$\beta = \frac{\left\{ (E-V)^2 - \left(E_0^2 + \frac{V^2}{2k} \right) \right\}^{\frac{1}{2}}}{E-V}. \quad \dots \quad (15)$$

We have then for the velocity (v_1) of the χ_1 wave

$$v_1 = c \cdot \frac{\left\{ (E-V)^2 - \left(E_0^2 + \frac{V^2}{2k} \right) \right\}^{\frac{1}{2}}}{E-V}. \quad \dots \quad (16)$$

As $p = \frac{m_0}{\sqrt{1-\beta^2}} \cdot v_1$ and the velocity of the χ_2 wave is p , we have for its value (when projected in the q -space) *

$$v_2 = \frac{E_c}{\sqrt{(E-V)^2 - \left(E_0^2 + \frac{V^2}{2k} \right)}}. \quad \dots \quad (17)$$

* Kar and Mukherjee, loc. cit.

Again, for the frequencies of the χ_1 and χ_2 waves (loc. cit.)

$$\left. \begin{aligned} \nu_1 &= \frac{1}{\hbar} \cdot \frac{(E-V)^2 - \left(E_0^2 + \frac{V^2}{2k}\right)}{E-V} = \frac{2E_{\text{kin}}}{\hbar}, \\ \nu_2 &= \frac{E}{\hbar}. \end{aligned} \right\} \quad . \quad (18)$$

If, with the above values of v and ν the time is eliminated from the wave equation, the χ_1 and χ_2 equations become identical and we have

$$\Delta\chi + \frac{4\pi^2}{c^2\hbar^2} \left[(E-V)^2 - E_0^2 - \frac{V^2}{2k} \right] \chi = 0, \quad . \quad (19)$$

differing from (2) by the correction term $\frac{V^2}{2k}$.

Taking the solution as in (3) the R-equation may be expressed in the same form as (4) with the values of A and B as in (6). The value of C will, however, be different. It is evidently

$$\left. \begin{aligned} C &= -l(l+1) + \alpha^2 Z^2 - \frac{\alpha^2 Z^2}{2(l+1)}, \quad \text{for +spin,} \\ &= -l(l-1) + \alpha^2 Z^2 - \frac{\alpha^2 Z^2}{2l}, \quad \text{for -spin,} \end{aligned} \right\} \quad . \quad (20)$$

where $\alpha = \frac{2\pi e^2}{ch}$, the fine structure constant.

Proceeding in the way well known in the wave-statistics, with the above modified value of C, we get

$$\sqrt{\frac{B}{-A}} = n_r + \sqrt{(l+\frac{1}{2})^2 - \alpha^2 Z^2 - \frac{\alpha^2 Z^2}{2(l+1)}} + \frac{1}{2}, \quad \text{for +spin,} \quad . \quad . \quad . \quad (21)$$

$$= n_r + \sqrt{(l-\frac{1}{2})^2 - \alpha^2 Z^2 - \frac{\alpha^2 Z^2}{2l}} + \frac{1}{2}, \quad \text{for -spin.} \quad . \quad . \quad . \quad (22)$$

Substituting for A and B, and after usual transformation:

$$W = -\frac{RhcZ^2}{n^2} - \frac{Rhc\alpha^2 Z^2}{n^4} \left(\frac{n}{l+1} - \frac{3}{4} \right), \quad s = +\frac{1}{2}, \quad (23)$$

$$= -\frac{RhcZ^2}{n^2} - \frac{Rhc\alpha^2 Z^2}{n^4} \left(\frac{n}{l} - \frac{3}{4} \right), \quad s = -\frac{1}{2}. \quad . \quad (24)$$

which are the well-known spin-relativity formulae of Sommerfeld-Dirac. For no spin the relativistic wave-statistical value known before is

$$W = -\frac{Rhcz^2}{n^2} - \frac{Rhca^2Z^2}{n^4} \left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4} \right). \dots \quad (25)$$

Therefore, subtracting (25) from (23) or (24), we can get the correction in energy due to spin.

Eigenfunctions (χ_1 , χ_2).—Let us consider the phase-space for a group of electrons moving in different Bohr orbits. On account of the two kinds of spin there will be two classes of phase-points distributed over the whole phase-space. Accordingly there must be two sets of eigenfunctions, viz. $(\chi_1)_1$, $(\chi_2)_1$ and $(\chi_1)_2$, $(\chi_2)_2$. If, however, we fix a direction in the space, the direction of motion in the orbit becomes material. In other words, we must distinguish between $+l$ and $-l$. Therefore we shall have to take two more sets of eigenfunctions, viz., $(\chi_1)_3$, $(\chi_2)_3$ and $(\chi_1)_4$, $(\chi_2)_4$. Here it should be noted that since $l(l+1)$ and $l(l-1)$ in the two R-equations do not take new values but simply interchange if $-l$ is put for $+l$, there will be no R-equations other than the two we have already taken.

The R-functions for $l_{\min.}=0$ and $l_{\min.}=1$ will henceforth be written as R_1 and R_2 . Again, when it is not necessary to emphasize the difference between χ_1 and χ_2 functions, we shall put

$(\chi)_1$ for $(\chi_1)_1$ or $(\chi_2)_1$; $(\chi)_2$ for $(\chi_1)_2$ or $(\chi_2)_2$, etc.

We are now in a position to write at once for the (χ) -functions

$$(\chi)_1 = C_1 R_1 P_l^m(\cos \theta) e^{im\phi}, \quad l_{\min.} = 0, \quad . \quad (26)$$

$$(\chi)_2 = C_2 R_2 P_{l-1}^m(\cos \theta) e^{im\phi}, \quad l_{\min.} = 1, \quad . \quad (27)$$

$$(\chi)_3 = C_3 R_2 P_{l-1}^{m-1}(\cos \theta) e^{i(m-1)\phi}, \quad l_{\min.} = 1, \quad . \quad (28)$$

$$(\chi)_4 = C_4 R_1 P_l^{m-1}(\cos \theta) e^{i(m-1)\phi}, \quad l_{\min.} = 0, \quad . \quad (29)$$

where C_1 , C_2 , etc., are constants to be evaluated and the associated Legendre functions in $(\chi)_1$, $(\chi)_4$ and $(\chi)_2$, $(\chi)_3$ satisfy the well-known differential equations :

$$\frac{d^2}{d\theta^2}(P_l^m) + \cot \theta \frac{d}{d\theta}(P_l^m) + \left\{ l(l+1) - \frac{m^2}{\sin^2 \theta} \right\} P_l^m = 0, \quad . \quad (30)$$

$$\frac{d^2}{d\theta^2}(P_l^{m-1}) + \cot \theta \frac{d}{d\theta}(P_l^{m-1}) + \left\{ l(l+1) - \frac{(m-1)^2}{\sin^2 \theta} \right\} \times P_l^{m-1} = 0. \quad (31)$$

$$\frac{d^2}{d\theta^2}(P_{l-1}^m) + \cot \theta \frac{d}{d\theta}(P_{l-1}^m) + \left\{ l(l-1) - \frac{m^2}{\sin^2 \theta} \right\} \times P_{l-1}^m = 0, \quad (32)$$

$$\frac{d^2}{d\theta^2}(P_{l-1}^{m-1}) + \cot \theta \frac{d}{d\theta}(P_{l-1}^{m-1}) + \left\{ l(l-1) - \frac{(m-1)^2}{\sin^2 \theta} \right\} \times P_{l-1}^{m-1} = 0. \quad (33)$$

We shall now proceed to find the interrelations between the constants C_1 and C_4 , C_2 and C_3 . This may be effected with the help of the fundamental condition that the resultant magnetic moment must be independent of the coordinates. This is also ensured by taking $m-1$ in place of m in the exponential with ϕ (vide (28), (29)).

The components of differential moment operators in polar coordinates well known in wave-statistics are :

$$\left. \begin{aligned} M_{12} &= \frac{h}{2\pi i} \frac{\partial}{\partial \phi} (\chi)^{m, l} = \frac{h m}{2\pi} (\chi)^{m, l}, \\ M_{23} &= \frac{h}{2\pi i} \left(\sin \phi \frac{\partial}{\partial \theta} + \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right) (\chi)^{m, l} = \frac{h}{4\pi} \\ &\quad \times [(\chi)^{m+1, l} + \{l(l+1) - m(m-1)\} (\chi)^{m-1, l}], \\ M_{31} &= \frac{h}{2\pi i} \left(\cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right) (\chi)^{m, l} = -\frac{h}{4\pi i} \\ &\quad \times [(\chi)^{m+1, l} - \{l(l+1) - m(m-1)\} (\chi)^{m-1, l}], \end{aligned} \right\}. \quad (34)$$

and for the resultant

$$\begin{aligned} M^2 &= M_{12}^2 + M_{23}^2 + M_{31}^2 = \left(\frac{h}{2\pi i} \right)^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \\ &= \left(\frac{h}{2\pi} \right)^2 l(l+1), \text{ for } (\chi)_1, (\chi)_4 \dots \quad (35) \end{aligned}$$

$$= \left(\frac{h}{2\pi} \right)^2 l(l-1), \text{ for } (\chi)_2, (\chi)_3. \quad (36)$$

Usually the value of $|M|$ is obtained from (35) or (36)

1000 Prof. K. C. Kar and Mr. K. K. Mukherjee on the
by boldly taking the square root of the right-hand side
to be $\frac{h}{2\pi}l$. The reason may be given below:—

If we take into account the spin of the electron, then (35) and (36) should become

$$\left(M \pm \frac{1}{2} \frac{h}{2\pi}\right)^2 = \left(\frac{h}{2\pi}\right)^2 j(j+1), \quad \dots, \quad (37)$$

$$= \left(\frac{h}{2\pi}\right)^2 j(j-1), \quad \dots. \quad (38)$$

where $j=l \pm \frac{1}{2}$. The left-hand side of (37), (38) may be easily shown to be

$$M^2 \pm \frac{h}{2\pi}M + \frac{3}{4}\left(\frac{h}{2\pi}\right)^2.$$

Hence from (37) we have

$$M = \frac{h}{2\pi} \quad \text{or} \quad \frac{h}{2\pi}(l+1).$$

But since $l_{\min.}=0$, we must take the latter value. In the same way from (38) we get

$$M = \frac{h}{2\pi}(l-1) \quad \text{or} \quad \frac{h}{2\pi}l.$$

Here again, as $l_{\min.}=1$, we shall take the second value. Thus we have *

$$\left. \begin{aligned} M &= \frac{h}{2\pi}(l+1), & s &= +\frac{1}{2}, \\ &= \frac{h}{2\pi}l, & s &= -\frac{1}{2}. \end{aligned} \right\} \quad \dots. \quad (39)$$

Having got the resultant moment for the two cases we can at once write for the moment equations for the four eigenfunctions:

$$M_{12}(\chi)_1 + M_{23}(\chi)_1 - iM_{31}(\chi)_1 = \frac{h}{2\pi}l(+1)(\chi)_1, \quad \dots \quad (40)$$

$$M_{12}(\chi)_2 + M_{23}(\chi)_2 - iM_{31}(\chi)_2 = \frac{h}{2\pi}l(\chi)_2, \quad \dots. \quad (41)$$

* Dirac takes l for both kinds of spin.

$$M_{12}(\chi)_3 - M_{23}(\chi)_3 - iM_{31}(\chi)_3 = -\frac{h\ell}{2\pi}(\chi)_3, \quad \dots \quad (42)$$

$$M_{12}(\chi)_4 - M_{23}(\chi)_4 - iM_{31}(\chi)_4 = -\frac{h(\ell+1)}{2\pi}(\chi)_4, \quad \dots \quad (43)$$

where $\sqrt{-1}$ is taken in the coefficient only to make it real (see equation (34)). Now, substituting for $(\chi)_1$, $(\chi)_4$ and adding (40) and (43), and finally, after transformation with the help of the well-known relations connecting two associated Legendre functions, viz.,*

$$\left. \begin{aligned} m \cot \theta P_l^m + \frac{\partial}{\partial \theta} (P_l^m) &= (l+m)(l-m+1) P_{l-1}^{m-1}, \\ -(m-1) \cot \theta P_l^{m-1} + \frac{\partial}{\partial \theta} (P_l^{m-1}) &= -P_l^m. \end{aligned} \right\} \quad (44)$$

We get

$$\{C_4 - C_1(l-m+1)\} \{P_l^m e^{i\phi} + (l+m)P_l^{m-1}\} R_1 e^{i(m-1)\phi} = 0, \quad (45)$$

which at once gives

$$C_4 = C_1(l-m+1). \quad \dots \quad (46)$$

In the same way, by combining (41) and (42) and with the help of (44), for $l=l-1$, we get

$$\{C_3 - C_2(l-m)\} \{P_{l-1}^m e^{i\phi} + (l+m-1)P_{l-1}^{m-1}\} R_2 e^{i(m-1)\phi}, \quad (47)$$

giving the relation

$$C_3 = C l_2(-m). \quad \dots \quad (48)$$

Thus the four unknown constants are reduced to two. But as only one other condition (viz., the normalizing—or rather, the “average”—condition) is left we shall assume $C_1 = C_2 = C$, which is determined from

$$C \int \{(\chi_1)_1(\chi_2)_1 + (\chi_1)_2(\chi_2)_2 + (\chi_1)_3(\chi_2)_3 + (\chi_1)_4(\chi_2)_4\} d\tau = 1. \quad (49)$$

The breaking up of one eigenfunction into four, viz., $(\chi)_1$, $(\chi)_2$, $(\chi)_3$, and $(\chi)_4$ is undoubtedly the effect of the electron spin. It will be shown just now that there is yet another effect of spin, which further slightly changes the values of (χ) 's already obtained. For this purpose let us consider the phase-space for a group of spinning electrons moving in orbits. The eigenfunctions obtained in (26)–(29) are really those for the orbital motion as

* Whittaker and Watson, ‘Modern Analysis,’ Cambridge.

affected by the spin. If, however, we suppose for a moment the orbital motion to be suppressed, the spinning motion still remains and we have a group of rotators. The finer variation of the phase density, assuming the rotators to have the lowest energy, is given by the corresponding eigenfunctions, and we have

$$(\chi) \sim P_0^0 e^{\frac{i}{2} \phi}, \quad P_0^0 = 1. \dots \dots \quad (50)$$

Hence from (26)–(29) and (50) we get by the principle of independent probabilities :

$$\left. \begin{aligned} (\chi)_1 &= CR_1 P_l^m (\cos \theta) e^{i(m+\frac{1}{2})\phi}, \\ (\chi)_2 &= CR_2 P_{l-1}^m (\cos \theta) e^{i(m+\frac{1}{2})\phi}, \\ (\chi)_3 &= C(l-m) R_2 P_{l-1}^{m-1} (\cos \theta) e^{i(m-\frac{1}{2})\phi}, \\ (\chi)_4 &= C(l-m+1) R_1 P_l^{m-1} (\cos \theta) e^{i(m-\frac{1}{2})\phi}. \end{aligned} \right\} \quad . \quad (51)$$

It should be noted that $m = m_l$, the orbital magnetic quantum number or the associated quantum number. The total magnetic quantum number is $m_l + m_s$, where $m_s = \pm \frac{1}{2}$, in Bohr unit.

The Phase-space: its Velocity Potential.—It follows from the foregoing discussions that in the phase-space for a group of electrons there are waves corresponding to the orbital motions and vortices corresponding to the spin. Thus the hydrodynamical analogy is complete. Now, outside the vortex-filaments which are evidently of the order of the size of the electrons, the motion is irrotational, and so a velocity potential exists in practically the whole of the phase-space. We are, however, concerned here with its value for the q -space. It is easily seen that the velocity potential ϕ satisfies the same differential equation as the wave-function χ_1 . We may therefore take $\phi = G \cdot \chi_1$ where G is a constant. Hence from the hydrodynamical theory the kinetic energy is given by

$$E_{\text{kin.}} = -\frac{1}{2} m G^2 \iiint \left\{ \left(\frac{\partial \chi_1}{\partial x} \right)^2 + \left(\frac{\partial \chi_1}{\partial y} \right)^2 + \left(\frac{\partial \chi_1}{\partial z} \right)^2 \right\} d\tau. \quad (52)$$

$$\begin{aligned} &= \frac{1}{2} m G^2 \iint \chi_1 \text{grad} \chi_1 dS + \frac{1}{2} m G^2 \iiint \chi_1 \Delta \chi_1 d\tau \\ &= \frac{1}{2} m G^2 \iiint \chi_1 \Delta \chi_1 d\tau, \quad \dots \dots \dots \quad . \quad (53) \end{aligned}$$

as the surface integral is zero. Again, from (1), we have

$$-\frac{h^2}{8\pi^2 m} \iiint \chi_1 \Delta \chi_1 d\tau = + \iiint (E - V) \chi_1^2 d\tau = E_{\text{kin}}. \quad (54)$$

Comparing (53) and (54) we have at once

$$G = \frac{h}{2\pi i m} \dots \dots \dots \quad (55)$$

Substituting this value of G in (52) we get the well-known wave-statistical value of kinetic energy. Again, we have for the velocity

$$\begin{aligned} v &= \iiint \chi \text{ grad } (G\chi) d\tau \\ &= \frac{h}{2\pi i m} \iiint \chi \text{ grad } \chi d\tau, \text{ from (55), } \dots \dots \end{aligned} \quad (56)$$

without distinguishing between χ_1 and χ_2 .

Or we have for the well-known value of momentum

$$p = \frac{h}{2\pi i} \iiint \chi \text{ grad } \chi d\tau, \quad \dots \dots \quad (57)$$

leading to the differential moment operators given in (34).

In the relativistic Kepler problem with spin we must use equation (19) instead of equation (1) as before. Therefore we have corresponding to (54)

$$-\frac{h^2}{8\pi^2 m} \iiint \chi \Delta \chi d\tau = \frac{1}{2mc^2} \left\{ (E - V)^2 - E_0^2 - \frac{V^2}{2k} \right\}. \quad (58)$$

Now, since the relativistic change of mass is not affected by spin, we have

$$mc^2 = \frac{E_0}{\sqrt{1 - \beta^2}} = E - V,$$

and equation (58) becomes

$$-\frac{h^2}{8\pi^2 m} \iiint \chi \Delta \chi d\tau = \frac{1}{2(E - V)} \left\{ (E - V)^2 - E_0^2 - \frac{V^2}{2k} \right\}. \quad (59)$$

It is very interesting to note that with this value of the relativistic kinetic energy we at once get the same frequency ν_1 of the χ_1 wave as intuitively taken in (18).

LXXXI. *The Strain Energy Method in Elastic Network Analysis: illustrated by an Application to the Portal Frame.* By E. H. BATEMAN, M.A.*

1. **S**OME solutions for a portal frame are worked out in three papers recently published †, and as this structure has been exhaustively analysed, as, for instance, by Gehler ‡, it affords a clear illustration of the advantage of a generalized strain-energy method. This system of determining the bending moments in an elastic network is simpler and more direct than the slope-deflexion or three-moment methods, and is, of course, of wider application than the latter, since it is not limited to frameworks which can be reduced to linear form.

2. The strain energy W in an elastic bar AB , of stiffness K , which is bent by any distribution of transverse loading and by end moments A and B , is given by

$6EKW = A^2 + AB + B^2 - A.(2a+b) - B.(2b+a) + C$, (1)
where E is Young's Modulus, a and b are the end moments at A and B which would be produced by the transverse loading if the ends of the bar were fixed in direction, and C is independent of A and B §.

The determination of the fixing moments a and b , in terms of the applied forces, presents as little difficulty as finding the corresponding expressions in the equation of three moments, *e. g.*, for a concentrated transverse load P , at a point distant x from A ,

$$a = Px \left(1 - \frac{x}{l}\right)^2, \quad b = Px \left(1 - \frac{x}{l}\right) \cdot \frac{x}{l},$$

and for a distributed load

$$a = \int_0^l wx \left(1 - \frac{x}{l}\right)^2 dx, \quad b = \int_0^l wx \left(1 - \frac{x}{l}\right) \cdot \frac{x}{l} dx,$$

where w is any function of x .

* Communicated by the Author.

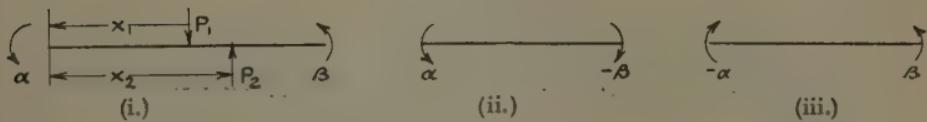
† C. E. Larard, "The General Solution of the Portal Frame," Phil. Mag., May 1931, p. 1104. V. D. Belfield, "Some Applications of the Theorem of Three Moments," Phil. Mag., March 1933, p. 562. F. C. Lea, "The Experimental Determination of the Forces and Moments in the Elements of Indeterminate Structures," Phil. Mag., May 1933, p. 881.

‡ W. Gehler, 'Der Rahmen,' Berlin, 1925.

§ E. H. Bateman, "The Strain Energy of an Elastic Bar," Phil. Mag., Dec. 1933, p. 1128.

Now, in equation (1) the values of A , B , a , b are of the same sign when they correspond to centres of curvature on the same side of the bar. Since, moreover W is a function of these moments in the second degree, it is evident that to ensure consistency of sign in writing down the total strain energy in a network it is sufficient to establish conformity between the directions in which the end moments and the fixing moments are measured in each bar of the network independently. There are, however, in a network the relations of statical equilibrium between the end moments in the bars and the moments of the external forces, and for convenience in formulating these relations the unknown quantities may be taken to be the terminal couples α , β , etc., all of which act in the same direction when of the same sign. Then the end moments may be written either α , $-\beta$, or $-\alpha$, β , and the signs of a and b will be determined by considering whether

Fig. 1.

(ii.) $A = \alpha$, $B = -\beta$,

$$a = P_1 x_1 \left(1 - \frac{x_1}{l}\right)^2 - P_2 x_2 \left(1 - \frac{x_2}{l}\right)^2,$$

$$b = P_1 x_1 \left(1 - \frac{x_1}{l}\right) \cdot \frac{x_1}{l} - P_2 x_2 \left(1 - \frac{x_2}{l}\right) \cdot \frac{x_2}{l}.$$

(iii.) $A = -\alpha$, $B = \beta$,

$$a = -P_1 x_1 \left(1 - \frac{x_1}{l}\right)^2 + P_2 x_2 \left(1 - \frac{x_2}{l}\right)^2,$$

$$b = -P_1 x_1 \left(1 - \frac{x_1}{l}\right) \cdot \frac{x_1}{l} + P_2 x_2 \left(1 - \frac{x_2}{l}\right) \cdot \frac{x_2}{l}.$$

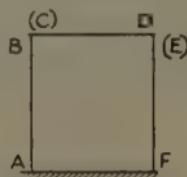
or not they are measured in the same direction as the corresponding end moments.

Thus in (i.) of fig. 1 a direction is assumed for the terminal couples acting on a bar AB , which carries the transverse loads P_1 and P_2 . In (ii.) and (iii.) of fig. 1 are shown the alternative methods of stating the bending moments for use in equation (1) and the values of A , B , a , b in the two cases are tabulated below the figure.

3. The complete solution for a portal frame, fig. 2, loaded in any manner, is now easily derived by the application of Castigliano's theorem of minimum strain energy.

The frame ABDF is formed by the three bars AB, CD, EF, rigidly connected together and fixed at A and F, and the terminal couples acting on the bars in the same direction may be taken as $\alpha, \beta; -\beta, -\delta; \delta, \eta$, respectively, since there is linear continuity at B, (C) and D, (E). Then the bending moments may be written $\alpha, -\beta; -\beta, \delta; \delta, -\eta$, and the transverse loading on the bars is described as in § 2 by the corresponding fixing-moment pairs, $a, b; c, d; e, f$.

Fig. 2.



Now, following (1), the total strain energy in the framework is

$$\begin{aligned} W = & l \{ \alpha^2 - \alpha\beta + \beta^2 - \alpha(2a+b) + \beta(a+2b) \} \\ & + m \{ \beta^2 - \beta\delta + \delta^2 + \beta(2c+d) - \delta(c+2d) \} \\ & + n \{ \delta^2 - \delta\eta + \eta^2 - \delta(2e+f) + \eta(e+2f) \} + C, \quad (2) \end{aligned}$$

where l, m, n are the values of $1/6EK$ for AB, CD, and EF.

The equations of equilibrium between the external forces and the terminal couples give the following relation:

$$\alpha + \beta + \delta + \eta + M = 0, \quad \dots \quad (3)$$

where M is the moment about A of the horizontal components of all the external forces in the direction of a positive terminal couple.

Since, therefore, $\alpha, \beta, \delta, \eta$ are not independent, only three equations will be required to establish the condition of minimum strain energy, and if these equations are written

$$0 = \frac{\partial W}{\partial \alpha} = \frac{\partial W}{\partial \beta} = \frac{\partial W}{\partial \delta}, \quad \dots \quad (4)$$

we have from (3)

$$\frac{\partial \eta}{\partial \alpha} = \frac{\partial \eta}{\partial \beta} = \frac{\partial \eta}{\partial \delta} = -1.$$

Then equations (4) become

$$\left. \begin{aligned} 0 &= l(2\alpha - \beta) - l(2a + b) + n(\delta - 2\eta) - n(e + 2f), \\ 0 &= l(2\beta - \alpha) + l(a + 2b) + m(2\beta - \delta) + m(2c + d) \\ &\quad + n(\delta - 2\eta) - n(e + 2f), \\ 0 &= m(2\delta - \beta) - m(c + 2d) + 3n(\delta - \eta) - 3n(e + 2f), \end{aligned} \right\} \quad (5)$$

and with (3),

$$0 = \alpha + \beta + \delta + \eta + M,$$

the values of α , β , δ , η can be found in terms of the applied forces as described by a , b , c , d , e , f , M .

The solution is

$$\frac{\alpha}{A} = \frac{\beta}{B} = \frac{\delta}{C} = \frac{\eta}{D} = \frac{1}{\Delta}, \quad \dots \quad (6)$$

where

$$\Delta = n(2m+n)(6l+m) + l(2m+l)(6n+m) + m(n-l)^2;$$

$$\begin{aligned} A &= -M \{ n(3l+m)(n+2m) + mn(n-l) \} \\ &\quad + la(2m^2 + 3n^2 + 6nl + 2lm + 17mn) \\ &\quad + lb(m^2 + 3n^2 + 12mn) + mc(2n^2 - 7nl - lm + 2mn) \\ &\quad + md(n^2 - 8nl - 3mn) + ne(m^2 + 3lm - 3nl - 3mn) \\ &\quad + nf(2m^2 + 5lm + 3nl + 2mn); \end{aligned}$$

$$\begin{aligned} B &= -M \{ 3nl(2m+n) \} - la(3n^2 + 6mn) \\ &\quad - lb(3n^2 + 6nl + 2lm + 5mn) \\ &\quad - mc(2n^2 + 11nl + 2lm + 2mn) - md(n^2 + 10nl) \\ &\quad + ne(-3nl + 4lm + mn) + nf(3nl + 6lm); \end{aligned}$$

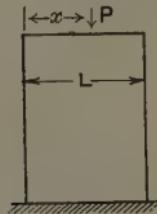
$$\begin{aligned} C &= -M \{ 3nl(2m+l) \} - la(3nl + 6mn) \\ &\quad - lb(-3nl + 4mn + lm) + mc(l^2 + 10nl) \\ &\quad + md(2l^2 + 11nl + 2mn + 2lm) \\ &\quad + ne(6nl + 2mn + 5lm + 3l^2) + nf(3l^2 + 6lm); \end{aligned}$$

$$\begin{aligned}
 D = & -M \{ l(3n+m)(2m+l) + ml(l-n) \} \\
 & - la(2m^2 + 3nl + 2lm + 5mn) - lb(m^2 - 3nl - 3lm + 3mn) \\
 & - mc(l^2 - 3lm - 8nl) - md(2l^2 + 2lm - 7nl - mn) \\
 & - ne(m^2 + 3l^2 + 12lm) - nf(2m^2 + 3l^2 + 6nl + 2mn + 17lm).
 \end{aligned}$$

4. As an example of a particular case, consider a symmetrical frame ($l=n$), loaded as in fig. 3. Here $a=b=e=f=0$, and $M=0$, while if the directions of positive terminal couples are as indicated in fig. 1(i.), we shall have

$$c = Px \left(1 - \frac{x}{L} \right)^2, \quad d = Px \left(1 - \frac{x}{L} \right) \cdot \frac{x}{L},$$

Fig. 3.



and the relation between the stiffnesses of the members may be written

$$l = n = m/\mu.$$

Then we find at once by substitution in (6),

$$\alpha = -Px \left(1 - \frac{x}{L} \right) \cdot \frac{\mu(5-\mu) + 2\mu(2\mu+1)x/L}{2(2\mu+1)(6+\mu)},$$

$$\beta = -Px \left(1 - \frac{x}{L} \right) \cdot \frac{\mu(13+4\mu) - 2\mu(2\mu+1)x/L}{2(2\mu+1)(6+\mu)},$$

$$\delta = Px \left(1 - \frac{x}{L} \right) \cdot \frac{11\mu + 2\mu(2\mu+1)x/L}{2(2\mu+1)(6+\mu)},$$

$$\eta = Px \left(1 - \frac{x}{L} \right) \cdot \frac{\mu(3\mu+7) - 2\mu(2\mu+1)x/L}{2(2\mu+1)(6+\mu)}.$$

5. In a symmetrical frame ($l=n$), loaded as in fig. 4, we have $c=d=e=f=0$, and with the same direction of positive terminal couples,

$$M = -Py, \quad a = Py \cdot (1 - y/H)^2, \quad b = Py \cdot (1 - y/H) \cdot y/H.$$

Then at once from (6),

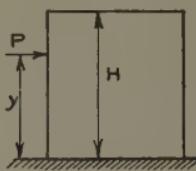
$$\alpha = Py \left\{ 1 - \frac{\mu+9}{2(6+\mu)} \cdot \frac{y}{H} - \frac{\mu+1}{2(1+2\mu)} \cdot \frac{y}{H} \cdot \left(1 - \frac{y}{H} \right) \right\},$$

$$\beta = Py \left\{ \frac{3}{2(6+\mu)} \cdot \frac{y}{H} - \frac{1}{2(1+2\mu)} \cdot \frac{y}{H} \cdot \left(1 - \frac{y}{H} \right) \right\},$$

$$\delta = Py \left\{ \frac{3}{2(6+\mu)} \cdot \frac{y}{H} + \frac{1}{2(1+2\mu)} \cdot \frac{y}{H} \cdot \left(1 - \frac{y}{H} \right) \right\},$$

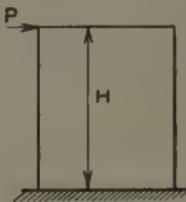
$$\eta = Py \left\{ \frac{\mu+3}{2(6+\mu)} \cdot \frac{y}{H} + \frac{\mu+1}{2(1+2\mu)} \cdot \frac{y}{H} \left(1 - \frac{y}{H} \right) \right\}.$$

Fig. 4.



6. The general solution for a frame acted on by a horizontal load at B, as indicated in fig. 5, is obtained from (6) by writing $a=b=c=d=e=f=0$ and $M=-PH$.

Fig. 5.



It is interesting to consider the ratio of the moments at the lower ends of the two columns; thus

$$\frac{\alpha}{\eta} = \frac{n}{l} \cdot \frac{2m^2 + m(5l+2n) + 3ln}{2m^2 + m(5n+2l) + 3ln},$$

or, if

$$\frac{n}{l} = \lambda, \quad \text{and} \quad \frac{m}{l} = \mu,$$

$$\frac{\alpha}{\eta} = \lambda \cdot \frac{2\mu^2 + \mu(5+2\lambda) + 3\lambda}{2\mu^2 + \mu(5\lambda+2) + 3\lambda}.$$

Then, considering the variation of μ , we find that the ratio $\frac{\alpha}{\eta}$ has a maximum or minimum value when

$$\mu = \sqrt{\frac{3\lambda}{2}},$$

and this value is

$$\frac{\alpha}{\eta} = \lambda \left\{ 1 - \frac{3(\lambda-1)\sqrt{3\lambda/2}}{6\lambda + (2+5\lambda)\sqrt{3\lambda/2}} \right\}.$$

The application of this result may be illustrated by a numerical example; thus, if $\lambda=3$, the value of μ for a critical value of $\frac{\alpha}{\eta}$ is

$$\mu = \frac{3}{\sqrt{2}},$$

which gives

$$\frac{\alpha}{\eta} = \lambda \cdot (1 - 0.235),$$

or, if $\lambda=6$, the corresponding values are

$$\mu = 3 \quad \text{and} \quad \frac{\alpha}{\eta} = \lambda \cdot (1 - 0.341),$$

and these determinations of the ratio $\frac{\alpha}{\eta}$ give the maximum error which would arise from the assumption that the external moment might be divided between the columns in proportion to their stiffnesses.

LXXXII. *Path and Stability of a Local Vortex moving round a Corner. (Second paper.) By ATSUSHI MIYADZU, Assistant Professor of Hydraulics and Hydrodynamics, Tohoku Imperial University, Sendai, Japan* *.

I. GENERAL.

PATH and stability of a free vortex maintained in a simple main flow round a corner have already been discussed † with respect to the domain bounded by two

* Communicated by the Author.

† A. Miyadzu, "Path and Stability of a Local Vortex moving round a Corner," Phil. Mag. xvi. pp. 553-562 (Sept. 1933).

straight lines, the inserted angle of which is $\alpha = \pi/n$. The present paper gives the more general result, deduced as applicable to any mode of the main flow under the same conditions, together with the special applications which include the case dealt with in my former paper as the simplest example.

The explanation of the process for deducing the results in this paper will be omitted as far as possible, for it, as also the notations * employed, are the same as those in the paper mentioned, to which reference may, if necessary, be made.

Let $F(t)$ denote, in general, the complex potential of the main flow in place of $-Ut$ in the former paper with reference to the t -plane, and w the complex potential for the flow with a local free vortex in it. The relations from equation (1) to (4) may be rewritten, so that

$$w = -\frac{i\Gamma}{2\pi} \log \left[(z^n - z_0^n) / (z^n - z_0^n) \right] + F(z^n),$$

$$w_v = -\frac{i\Gamma}{2\pi} \log \left[(z^n - z_0^n) / (z^n - z_0^n) (z - z_0) \right] + F(z^n)$$

$$= \frac{i\Gamma}{2\pi} \log \left[(t^n - t_0^n) / (t - t_0) \right] + F(t),$$

and

$$\begin{aligned} -u_i + iv_i &= \left(\frac{dw}{dt} \right)_{t=t_0} = \frac{i\Gamma}{2\pi} \left[\frac{(1-n)}{2nt_0} + \frac{1}{t_0 - \bar{t}_0} \right] + \left(\frac{dF}{dt} \right)_{t=t_0} \\ &= \frac{i\Gamma}{2\pi} \left[\frac{(1-n)}{2nt_0} + \frac{1}{t_0 - \bar{t}_0} \right] + \frac{dF(t_0)}{dt_0}, \end{aligned}$$

provided that the function $F(t)$ is primarily free from t_0 , which denotes the position of a vortex. Splitting $F(t_0)$ into real and imaginary parts respectively, and putting

$$t_0 = x + iy = re^{i\theta}, \quad F(t_0) \equiv R + iI, \quad \dots \quad (1)$$

* It is to be remarked here that in the former paper the use of the notation “ t ” varies in the two parts, that is, up to equation (5a) “ t ” represents the fundamental complex plane as first pointed out, while as used afterwards, without notice, in equations (5b), (11), (12), and (13) “ t ” represents the usual period of time.

we obtain

$$u_t = -\frac{\Gamma}{4\pi r} \left[\frac{1-n}{n} \sin \theta + \frac{1}{\sin \theta} \right] - \frac{\partial R}{\partial x},$$

$$v_t = \frac{\Gamma}{4\pi r} \cdot \frac{1-n}{n} \cos \theta + \frac{\partial I}{\partial x}.$$

Since

$$\frac{\partial}{\partial x} = \cos \theta \cdot \frac{\partial}{\partial r} - \sin \theta \cdot \frac{\partial}{r \partial \theta},$$

$$\frac{\partial R}{\partial r} = \frac{1}{r} \frac{\partial I}{\partial \theta}, \quad \frac{1}{r} \frac{\partial R}{\partial \theta} = -\frac{\partial I}{\partial r},$$

the polar velocity components in the t -plane are

$$V_r = -\frac{\Gamma}{4\pi r} \cot \theta - \frac{1}{r} \frac{\partial I}{\partial \theta},$$

$$V_\theta = \frac{\Gamma}{4\pi r n} - \frac{\partial I}{\partial r}.$$

Eliminating the time "t" between them as in the former paper and integrating it, we have

$$\frac{\Gamma}{4\pi} \log(r \sin^n \theta) + nI = C_1.$$

Taking the relations $r = \rho^n$, $\theta = n\phi$ as before, it may be written as

$$\frac{\Gamma}{4\pi} \log(\rho \sin n\phi) + I = C. \quad \dots \quad (2)$$

This is the final expression of the path of a local vortex in the z -plane, maintained in a main flow which may be of any type generally represented by function F .

The velocity components are obtained by

$$\begin{aligned} -u_z + iv_z &= (-V_r + iV_\theta) e^{-i\phi} = \left(\frac{dw}{dz} \right)_{z=z_0} \\ &= \frac{i\Gamma}{2\pi} \left[\frac{1-n}{2z_0} + \frac{nz_0^{n-1}}{z_0^n - z_0^n} \right] + \frac{dF(z_0^n)}{dz_0}. \end{aligned}$$

Putting

$$\frac{(F dz_0^n)}{dz_0} \equiv [R] + i[I], \quad \dots \quad (3)$$

we get

$$\left. \begin{aligned} u_z &= -\frac{\Gamma}{4\pi\rho} \left[(1-n)\sin\phi + \frac{n\cos(n-1)\phi}{\sin n\phi} \right] - [R], \\ v_z &= \frac{\Gamma}{4\pi\rho} \left[(1-n)\cos\phi + \frac{n\sin(n-1)\phi}{\sin n\phi} \right] + [I], \\ V_p &= -\frac{n\Gamma}{4\pi\rho} \cot n\phi - \frac{\partial R}{\partial \rho}, \\ V_\phi &= \frac{\Gamma}{4\pi\rho} + \frac{\partial I}{\partial \rho}. \end{aligned} \right\} \quad \dots \quad (5)$$

These may be rewritten in the appropriate form by making use of the well-known relations such as

$$\frac{\partial R}{\partial \rho} = \frac{1}{\rho} \frac{\partial I}{\partial \phi}, \quad \frac{1}{\rho} \frac{\partial R}{\partial \phi} = -\frac{\partial I}{\partial \rho}.$$

II. APPLICATIONS.

In applying the results obtained above, let us take the mode of the main flow in the form

$$F(t) = -U t^m = -U z^m.$$

The domain under consideration in the z -plane is, of course, bounded by two straight lines, the inserted angle of which is π/n ($1/2 \leq n < \infty$); m will be assumed to be an integral number, so that the real axis of the fundamental t -plane may become a boundary. The mode of the main flow changes its feature relatively to m , yet a few applications with respect to a positive integer m will be treated here in connexion with the former paper already mentioned. Then the main flow has such a mode that the domain is divided into m -equal parts, and certain stream lines in it stagnate on the boundary. This point of stagnation coincides with the corner of the boundary in this case as shown in fig. 1, but it is easily seen that this point may be arbitrarily taken at any point z_1 on the boundary in the z -plane, if we use the function of the main flow in the form

$$F(t) = -U(t-a)^m = -U(z^n - z_1^n)^m,$$

where a represents a real constant, positive or negative,

corresponding to z_1 (about this example further treatment is omitted in this paper).

Fig. 1 a.

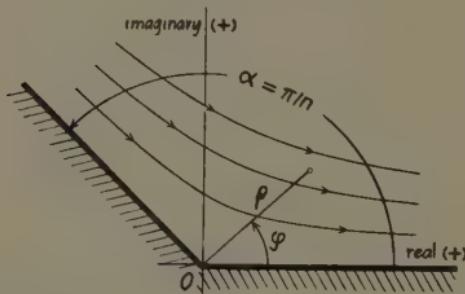
 $m = 1$ 

Fig. 1 b.

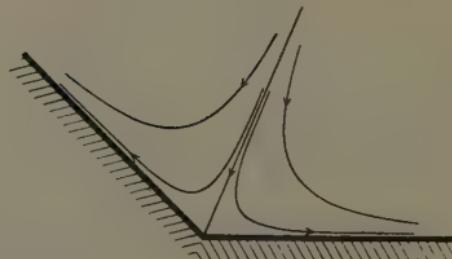
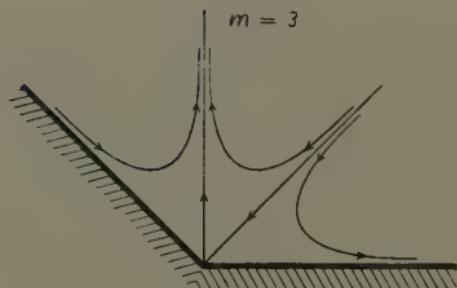
 $m = 2$ 

Fig. 1 c.

 $m = 3$ 

Now, in equations (1) and (3),

$$F_{z=z_0} = -U z_0^{mn},$$

$$R = -U \rho^{mn} \cos mn\phi, \quad I = -U \rho^{mn} \sin mn\phi,$$

and

$$\frac{d\mathbf{F}_{z=z_0}}{dz_0} = -mn\mathbf{U}z_0^{mn-1},$$

$$[\mathbf{R}] = -mn\mathbf{U}\rho^{mn-1} \cos(mn-1)\phi,$$

$$[\mathbf{I}] = -mn\mathbf{U}\rho^{mn-1} \sin(mn-1)\phi,$$

then, substituting these into the general results, we have path of a vortex;

$$\frac{\Gamma}{4\pi} \log(\rho \sin n\phi) - \mathbf{U}\rho^{mn} \sin mn\phi = C \quad \dots \quad (6)$$

velocity components;

$$u = -\frac{\Gamma}{4\pi\rho} \left[(1-n)\sin\phi + \frac{n\cos(n-1)\phi}{\sin n\phi} \right. \\ \left. + mn\mathbf{U}\rho^{mn-1} \cos(mn-1)\phi, \right] \quad \dots \quad (7)$$

$$v = \frac{\Gamma}{4\pi\rho} \left[(1-n)\cos\phi + \frac{n\sin(n-1)\phi}{\sin n\phi} \right. \\ \left. - mn\mathbf{U}\rho^{mn-1} \sin(mn-1)\phi, \right]$$

or

$$\left. \begin{aligned} \mathbf{V}_\rho &= -\frac{n\Gamma}{4\pi\rho} \cot n\phi + mn\mathbf{U}\rho^{mn-1} \cos mn\phi, \\ \mathbf{V}_\phi &= \frac{\Gamma}{4\pi\rho} - mn\mathbf{U}\rho^{mn-1} \sin mn\phi. \end{aligned} \right\} \quad \dots \quad (8)$$

Graphical Representation.

$m=1$.—It will be remembered that this case has already been dealt with in the former paper, and consequently no additions will be needed.

$m=2$.—The paths of a vortex calculated numerically are shown in fig. 2 and fig. 3 corresponding to the main flow in fig. 1B.

The paths of a vortex with the counter-clockwise circulation may easily be considered to be represented by the symmetrical curves of those shown in fig. 2 or fig. 3 with respect to the line bisecting the inserted angle of the domain.

$m=3$.—Fig. 4 and fig. 5 show the examples for $n > 1$ and $n < 1$ respectively.

From the condition for equilibrium

$$u_z = 0, v_z = 0 \quad \text{or} \quad V_\rho = 0, V_\phi = 0,$$

Fig. 2.

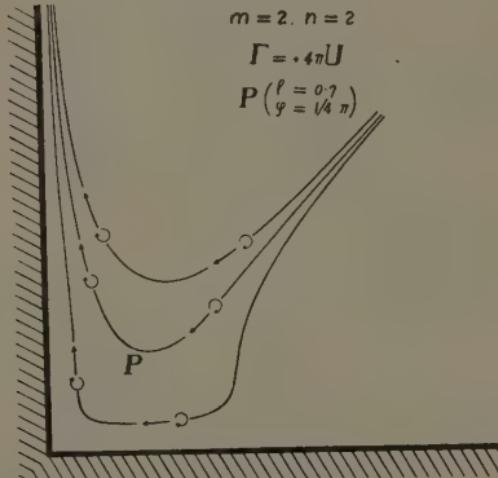
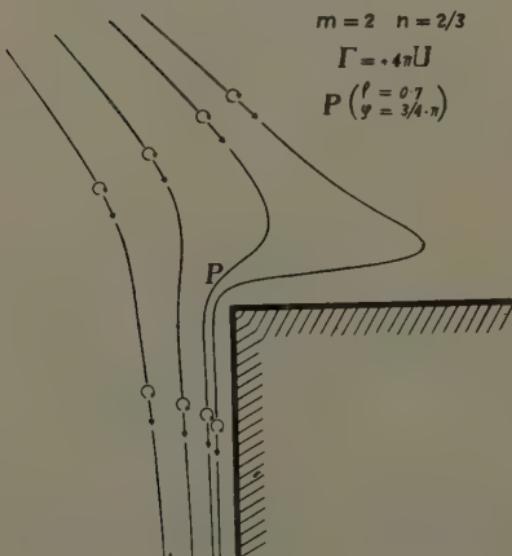


Fig. 3.



we have

$$\Gamma = 4\pi mnU \rho^m \sin mn\phi, \quad \dots \quad (9a)$$

$$n \cos n\phi \sin mn\phi = \sin n\phi \cos mn\phi. \quad \dots \quad (9b)$$

$m=1$.—This case is omitted, since it also has already been discussed in my former paper.

$m=2$.—From equation (9b), we get

$$[(n-1) \cos 2n\phi + n] \sin n\phi = 0. \quad \dots \quad (10a)$$

Fig. 4 A.

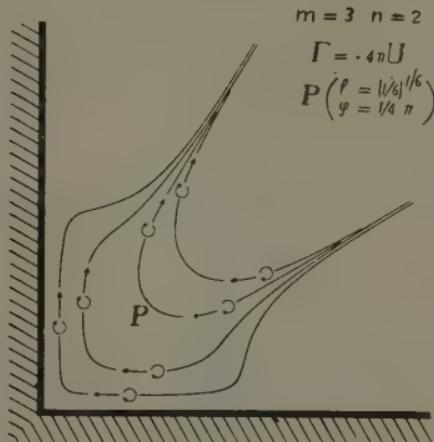
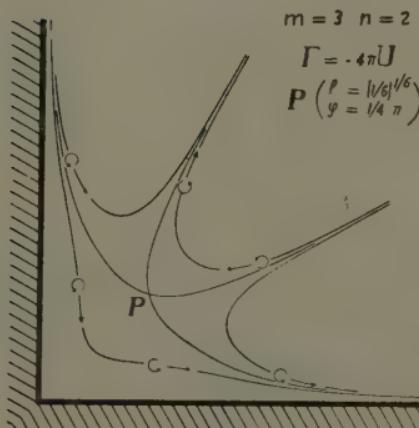


Fig. 4 B.



As the vortex cannot be considered to exist on the boundary $\phi=0$ or $\phi=\pi/n$, it results that $\sin n\phi \neq 0$, and we get

$$\cos 2n\phi = \frac{n}{1-n}. \quad \dots \quad (10b)$$

On the other hand, we have

$$|n/(1-n)| \geq 1 \text{ for } 1/2 \leq n < \infty.$$

Fig. 5 A.

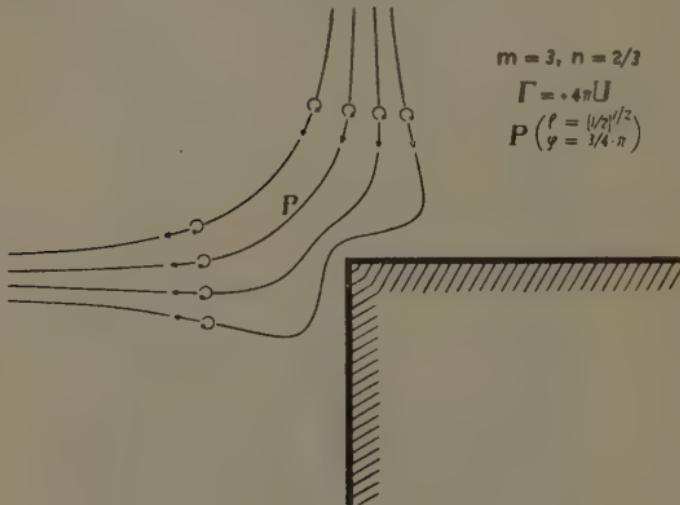
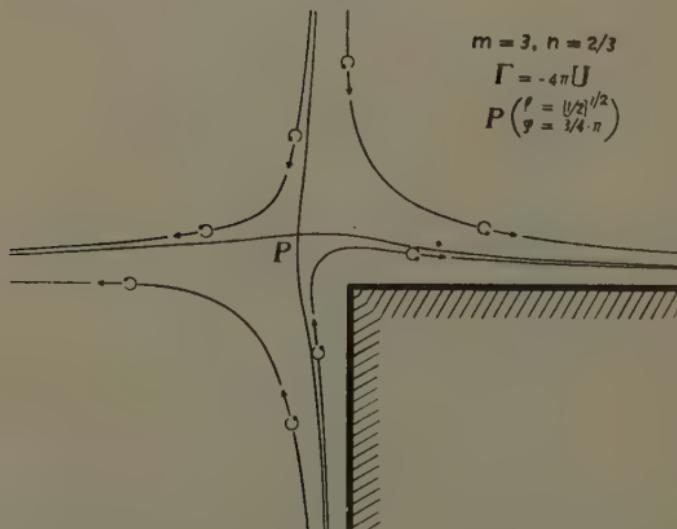


Fig. 5 B.



Hence $n = 1/2$ alone satisfies the equation (10b), which is reduced to

$$\cos \phi = 1. \quad . \quad . \quad . \quad . \quad . \quad (10c)$$

From this we get $\phi=0$ or 2π ; these represent, of course, the other two sides of a straight boundary on which a vortex is not considered to exist as before. The position of equilibrium is not obtained in this case.

$m=3$.—Equation (9b) gives

$$[n+1-2(1-n)\cos 2n\phi]\sin 2n\phi=0, \dots \quad (11)$$

from which we obtain

$$\sin 2n\phi=0, \text{ or } \cos 2n\phi=(n+1)/2(1-n). \quad (11a) \text{ or } (11b)$$

(A) From (11a)

$$\phi=\pi/2n, \dots \quad (12a)$$

substituting this into (9a), we get

$$\Gamma=-12\pi n U \rho^{3n} \dots \quad (12b)$$

That is, a vortex may reach a state of equilibrium on the line bisecting the inserted angle of the domain as in the case of $m=1$, but when a vortex has a counter-clockwise circulation of the magnitude $12\pi n U \rho^{3n}$ in the main flow shown in fig. 1c.

(B) Equation (11b) affords another relation giving the positions of equilibrium. Since the limitation $1/2 \leq n < \infty$ was first assumed, it follows that:

For $1/2 \leq n \leq 1$, the right-hand side of equation (11b) becomes greater than unity, and it does not hold good.

For $n > 1$ we get $2(1-n)=2(n-1)$; hence in this case we may solve equation (11b) under the condition

$$n+1 \leq 2(n-1) \quad \text{or} \quad n \geq 3, \dots \quad (13)$$

(1) $n=3$.—Equation (11b) becomes $\cos 6\phi=-1$, from which we get $\phi=\pi/6$; this is no other than the result obtained already in case of (A).

(2) $n=4$.—Equation (11b) becomes $\cos 8\phi=-5/6$, from which we get

$$\phi=22^\circ 30' \pm 4^\circ 12'; \dots \quad (14a)$$

substituting this into (9a), we have

$$\Gamma=-\frac{16}{3}\sqrt{33}\pi U \rho^{12} \dots \quad (14b)$$

For n greater than 4, the similar examination will be

necessary to derive a definite conclusion regarding it, but it may be summarized here, such that

for $m=3$.

(1) The point on the line bisecting the inserted angle of the domain can become a position of equilibrium with respect to all values of n limited within $1/2 \leq n < \infty$.

(2) If n is greater than 3 the other positions of equilibrium are possible to exist besides the one in case of (1).

The present writer will not stop to examine closely the numerous special results for n or m left untouched here, together with the other types of the main flow, but proceed to discuss the stability of a vortex at the positions of equilibrium obtained above and conclude this paper.

Let ξ and η denote the radial and transversal displacements of a vortex from the position of equilibrium, referred to the polar coordinates ρ and ϕ , with the same assumption as before, that both ξ and η are so small that the square and product of them are negligible. The equations of the disturbed motion then become

$$\left. \begin{aligned} \frac{d\xi}{dt} &= L\xi + M\eta, \\ \frac{d\eta}{dt} &= N\xi + K\eta, \end{aligned} \right\} \quad \dots \quad (15)$$

where

$$\left. \begin{aligned} L &= \left\{ \frac{\partial V\rho}{\partial \rho} = \frac{n\Gamma}{4\pi\rho^2} \cot n\phi + mn(mn-1)U\rho^{mn-2} \cos mn\phi, \right. \\ M &= \left. \frac{\partial V\rho}{\partial \phi} = \frac{n^2\Gamma}{4\pi\rho^2} \operatorname{cosec}^2 n\phi - m^2n^2U\rho^{mn-2} \sin mn\phi, \right. \\ N &= \left. \frac{\partial V\phi}{\partial \rho} = -\frac{\Gamma}{4\pi\rho^2} - mn(mn-1)U\rho^{mn-2} \sin mn\phi, \right. \\ K &= \left. \frac{\partial V\phi}{\partial \phi} = -m^2n^2U\rho^{mn-2} \cos mn\phi. \right. \end{aligned} \right\} \quad \dots \quad (16)$$

with the conditions for equilibrium.

$m=1$.—The conditions for equilibrium are

$$\phi = \pi/2n, \quad \Gamma = 4\pi n U \rho^n,$$

which give

$$L=0, \quad M=n^2(n-1)U\rho^{n-2}, \quad N=-n^2U\rho^{n-2} \quad \text{and} \quad K=0. \quad \dots \quad (17)$$

Then equation (15) is transformed into

$$\frac{d^2(\xi, \eta)}{dt^2} = MN(\xi, \eta) = (1-n)n^4U^2\rho^{2n-4}(\xi, \eta) \quad \dots \quad (18)$$

In my former paper this result was already derived referring to Cartesian coordinates and discussed.

$m=2$.—The equilibrium position does not exist.

$m=3$.

1. For all values of $n (1/2 \leq n < \infty)$,

$$\phi = \pi/2n, \quad \Gamma = -12\pi n U \rho^{3n},$$

$$L=0, \quad M=3(3-n)n^2U\rho^{3n-2}, \quad N=9n^2U\rho^{3n-2}, \quad K=0, \quad (19)$$

and

$$\frac{d^2(\xi, \eta)}{dt^2} = MN(\xi, \eta) = 27(3-n)n^4U^2\rho^{6n-4}(\xi, \eta). \quad (20)$$

This shows that the equilibrium is stable, neutral, or unstable for the region $\alpha < = \text{or} > \pi/3$, since the coefficient of its right-hand side becomes $-$, 0 or $+$ for $n > =$ or < 3 and α is equal to π/n .

2. For $n=4$,

$$\left. \begin{aligned} \cos 8\phi &= -5/6 (\phi = 22^\circ 30' \mp 4^\circ 12'), \quad \Gamma = -\frac{16}{3} \sqrt{33} \pi U \rho^{12}, \\ L &= -K = \mp 64\sqrt{3} U \rho^{10}, \quad M = -\frac{80}{11} \sqrt{33} U \rho^{10}, \\ N &= 16\sqrt{33} U \rho^{10}, \end{aligned} \right\} \quad \dots \quad (21)$$

and

$$\frac{d^2(\xi, \eta)}{dt^2} = (L^2 + MN)(\xi, \eta) = 8448U^2\rho^{20}(\xi, \eta). \quad \dots \quad (22)$$

The equilibrium is obviously unstable.

Equation (20) suggests that the path of a vortex will show the characteristic feature depending upon n being greater or less than 3. The paths traced numerically are shown in fig. 6.

It is seen that the stable equilibrium position (P in fig. 6C) is confined to the space where a vortex moves describing a closed curve, while the unstable one (P in figs. 6A, 6B, or P_1 , P_2 in fig. 6C) corresponds to the point

Fig. 6 A.-

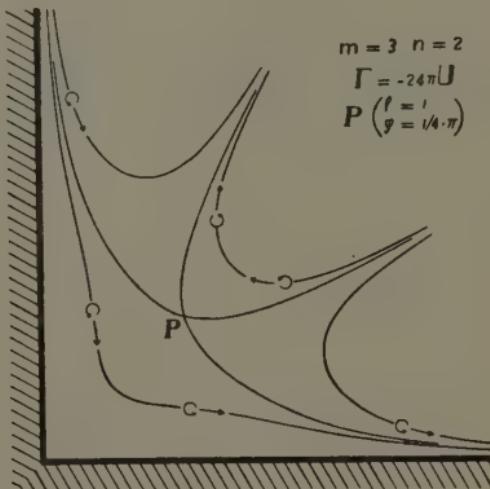
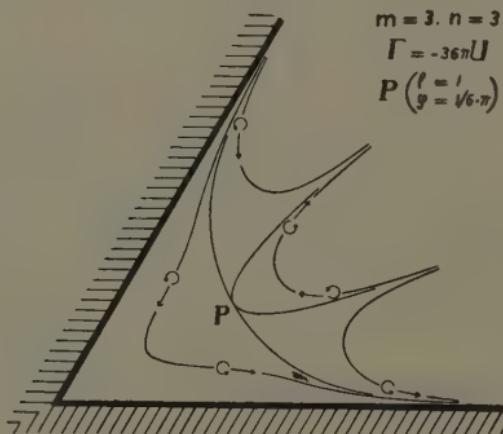


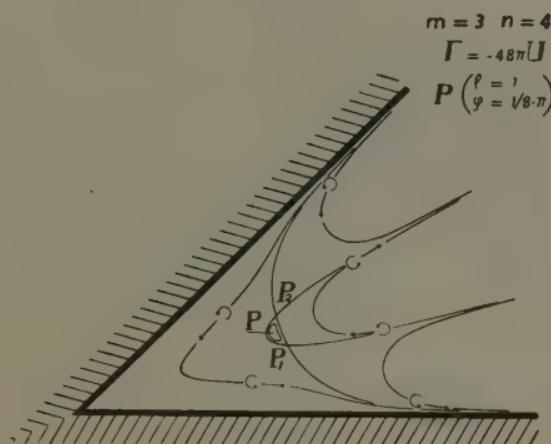
Fig. 6 B.-



of intersection of curves dividing the domain under consideration into several parts in which a vortex with the same strength of counter-clockwise circulation moves describing the peculiar form of the path respectively.

The similar conclusion can be deduced also in the case dealt with in the former paper.

Fig. 6 c.



In conclusion, the writer wishes to express his hearty thanks to Prof. O. Miyagi for his kind advice and encouragement, and also to Messrs. K. Tsunoda and T. Tanabe for their zealous help in numerical calculations.

Sendai.
Nov. 1st, 1933.

LXXXIII. *Note on the Deuton and Disintegration.* By HAROLD J. WALKE, B Sc., Mardon Research Scholar, University College, Exeter.†

IN a recent paper ‡ an explanation was offered of the emission of positive electrons accompanying the neutrons of aluminium as found by Curie and Joliot §. While this paper was in the press more recent work by these investigators || has definitely confirmed this positron emission, as they have observed, by means of a Wilson

† Communicated by Prof. F. H. Newman, D.Sc.

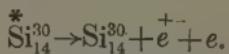
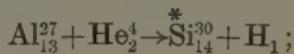
‡ Phil. Mag. xvii. p. 793 (1934).

§ Comptes Rendus, cxvii. p. 1885 (1933).

|| Ibid. cxviii. p. 264 (1934).

expansion chamber, positive electron tracks resulting from the bombardment of aluminium by α -particles.

Curie and Joliot explain this effect as due to the radioactivity of the unstable isotope formed, viz., P_{15}^{30} , this radioactivity taking the form of positron emission from the nucleus. This would seem to require, as a free nuclear component, the positive electron, for if we suppose that the radioactivity takes the form of internal conversion of γ -radiation within the nucleus, *i. e.*, in the negative field, negative electrons would be emitted as in the case of the β -ray disintegration of radioactive nuclei, the resultant nucleus being S_{16}^{30} . They also considered the possibility that the reaction was such that a proton was emitted, the positrons resulting from conversion of γ -radiation, emitted by an excited S_{14}^{30} nucleus in its return to the stable state Si_{14}^{30} , the action being:—



They could find, however, no reason why the negative electrons should not be detected if this action occurred, yet they were unable to detect such electrons. They concluded, therefore, that the positrons result from the neutron emission, the isotope P_{15}^{30} being radioactive.

The explanation offered in the author's previous paper does not depend upon this new type of radioactivity, since it is postulated that the return to the stable isotope is due to the conversion of γ -radiation in the positive potential field; but the negative electron is attracted to the nucleus, where it unites with the bound positive electron of the proton, it being assumed that the neutron is a simple particle, the proton being complex and consisting of a neutron and positron in close combination. As a result, the two electrons disappear in the form of quanta of γ -radiation, of energy about half a million volts. It is significant that Savel \dagger has detected γ -radiation accompanying the neutrons emitted by aluminium of energy 550,000 electron-volts.

\dagger *Ibid.* excviii. p. 370 (1934).

LXXXIV. *The Two Kinds of H_3 .*
*By Sir J. J. THOMSON, O.M., F.R.S.**

[Plate XXI.]

ABSTRACT.

I FOUND, more than twenty years ago, that certain solids when vigorously bombarded by cathode rays gave out a gas whose molecular weight is 3. This gas was permanent, and behaved like a molecule of normal hydrogen in that it disappeared when drawn slowly over red-hot copper oxide or when sparked strongly with oxygen; it also passed through tubes of hot palladium. Several chemists have since observed another modification of hydrogen with the same mass; this, which is very short-lived, was obtained from ordinary hydrogen.

This paper contains an account of experiments which confirm the existence of both the permanent and the fugitive H_3 and show how the amount of the permanent may be determined. The method used in these experiments was, in addition to taking the photographs showing the parabolas, to measure by the methods described in 'Rays of Positive Electricity,' p. 120, 2nd edition, the charges of electricity carried by the particles forming each parabola. In this way an estimate could be formed of the relative number of particles in the parabolas corresponding to H_1 , H_2 , H_3 . The difference in the properties of the H_3 from pure hydrogen and that got by bombardment is very remarkable. Fig. 1 (Pl. XXI.) represents the parabolas obtained from pure hydrogen. The top one is due to H_1 , the one below this to H_2 , and the one below this to H_3 . There is quite a strong (3) parabola, but the electrical method showed that practically all the particles producing this parabola had lost their charges before striking against the photographic plate; the charge carried by them was less than 1/8500 of the charge carried by the particles in the H_2 parabola. This indicates that the permanent H_3 in normal hydrogen is less than 1/8500 of the normal H_2 .

The parabolas for the gas obtained by bombarding KHO are shown in fig. 2 (Pl. XXI.). Though the (3) parabola is not so strong as in fig. 1, the charges carried by the

* Communicated by the Author.

particles in this parabola are very much greater, and are large enough to be measured without difficulty. The charge carried by the (3) particles was in one sample of gas 1/720 of that carried by the H₂ particles, and in another sample 1/480.

ONE of the first results obtained with the positive-ray method of chemical analysis was the discovery of particles having a mass three times that of an atom of hydrogen. These were first detected when the electric discharge passed through pure hydrogen, but their appearance was capricious, and I found they occurred with much greater regularity when the discharge passed through the gas evolved when certain solids were bombarded vigorously by cathode rays. The H₃ I obtained from this source was a permanent gas. There were, however, indications which led me to suspect that there were two kinds of H₃. Several chemists have since detected a modification of hydrogen with the mass corresponding to H₃, but having a very short life; this was obtained from normal hydrogen. I have lately been experimenting with the discharge through normal hydrogen, and find that by adjusting the conditions of the discharge it is possible to get strong parabolas corresponding to the mass 3, and have made a series of experiments to compare the behaviour of this form of H₃ with that obtained when solids are bombarded with cathode rays.

The method I used was to supplement the photographs showing the usual parabolas with measurement of the electric charge carried in a given time by the particles producing each parabola. I did this by the method described in 'Rays of Positive Electricity,' p. 120, 2nd edition. The method is to cut in the back of the vertical box in which the photographic plate can be moved up and down a parabolic slit of the same shape and size as one of the parabolas on the photographic plate. Behind the slit is a Faraday cylinder shaped so as just to catch all the particles which pass through it; this cylinder will receive per second a charge of electricity equal to that carried by the particles which produce the parabola. This charge was measured, as in the earlier experiments, by a Wilson tilted electrometer, but the accuracy of the readings was much improved by fixing a spur made of a short piece of a fibre of fine glass wool at the end of the

strip of gold leaf; the position of this can be read more accurately than that of the edge of the gold leaf which was what was read in the earlier experiments. With the spur the deflexions could be read without difficulty to $\cdot 1$ of a scale-division. I also measured in the same way the charge which passed through a circular hole at the place the rays strike when they are not deflected by electric or magnetic forces. This proved very useful, both as a test of the constancy of the discharge and also in adjusting the pressure and other conditions of the discharge so as to get the maximum current through the discharge-tube. The other changes made were to exhaust by one of the diffusion oil pumps made by Metropolitan Vickers Co. instead of by charcoal cooled by liquid air. I also replaced the fine tube used to get a thin stream of rays by a much larger cylindrical tube, closed at each end by metal disks at right-angles to its axis, with fine holes bored at their centres.

When making the electrical measurements the photographic plate was raised until it did not obstruct the path of positive rays to the slit.

By altering the magnetic force used to deflect the positive rays one parabola after another could be brought on the slit, the force required to bring a parabola due to a mass m on the slit being proportional to \sqrt{m} . Thus the magnetic forces required to bring the parabolas corresponding to H_1 , H_2 , H_3 , H_4 on the slit are in the proportion of 1, $1\cdot41$, $1\cdot73$, 2. The magnetic force was produced by an electromagnet, and within the range of forces used, proportional to the current through the magnet. When there was not a parabola on the slit the electrometer deflexion did not amount to $\cdot 1$ division in 2 minutes, while with a strong parabola on the slit it moved as much as 30 divisions in 1 second.

In the experiments the magnetic force was gradually raised, starting from below the value required to bring the parabola H_1 on the slit. The first deflexion occurred when H_1 reached the slit; a small percentage increase of the current made the deflexion rise from zero to a maximum and then vanish; further increase produced no deflexion until the force reached $1\cdot4$ times the value for the first deflexion. H_2 then came on the slit and there was a large deflexion. After passing this there was no deflexion until H_3 was reached, and so on.

After making the electrical measurements, the photographic plate was lowered into position and a photograph taken. Comparison of the photographs with the electrometer readings showed remarkable differences between the discharge through pure hydrogen and that through the gas emitted when solids are bombarded. In the first case the particles of H_2 which were positively electrified when they entered the electric and magnetic fields have lost their charges before they reach the slit, and do not produce a measurable deflexion of the electrometer, while in the second case enough of these retain their positive charge to produce a deflexion which can be measured with ease.

H_3 from Normal Hydrogen.

Fig. 1 (Pl. XXI.) is a photograph showing the parabolas when the discharge passed through hydrogen obtained by passing hydrogen from the oxy-hydrogen flame through a hot palladium tube. It will be seen that the H_3 parabola is well marked and by no means negligible in comparison with the parabolas due to H_1 , H_2 .

The result of the measurement of the charges by the electrical method was that when the H_1 parabola was on the slit the maximum deflexion was equal to 23.8 divisions in 15 seconds and occurred when the current through the electromagnet was .155 amp.

When the H_2 parabola was brought on the slit the maximum deflexion occurred when the current was .210 amp., and was equal to 58 divisions in 2 seconds. After the H_2 parabola had been driven across the slit there was no measurable deflexion until the arrival of parabolas due to carbon and oxygen. The region where the H_3 parabola would be brought on the slit, *i. e.*, when the current through the electromagnet was round about .27, was very carefully explored, and though a deflexion of .2 division per minute could easily have been detected, no trace of a deflexion was observed. The positive particles must have lost their charge, *i. e.*, gained an electron before reaching the plates. The photograph itself shows this loss of charge, for it will be noticed that the H_3 parabola has a strong straight secondary reaching to the origin, and it is the only parabola which has this. This secondary shows that some of the particles begin to lose their charge as soon as they enter the electric

and magnetic fields, and continue to do so while they are passing through them; those which retain their charges until they get through will strike the plate on the H₃ parabola, whether they have lost their charges or not, after leaving the fields. Since the distance they have to travel before they reach the photographic plate is much greater than the length of the fields, it is not surprising that by the time they reach the plate they have lost their charge.

Taking .2 division per minute as a deflexion which could be detected with certainty, then, since the deflexion due to the hydrogen molecules per minute was 58×30 , the ratio of the number of particles of permanent H₃ to the number of molecules of normal hydrogen must be less than 1:8700. This gives us the measure of the amount of permanent heavy hydrogen in the normal gas. It confirms also the existence of a short-lived form of H₃.

Gas obtained by bombarding Potash.

The photograph of the parabolas when the discharge went through this gas is shown in fig. 2 (Pl. XXI.). The H₃ line, though visible, is not so strong as that given in fig. 1 (Pl. XXI.) for pure hydrogen, yet the deflexions obtained in the electrical tests are very much greater, and can be detected without difficulty. The numbers in this case are: the parabola for H₁ gives the maximum deflexion 16 divisions in 30 seconds when the current through the magnet is .16 amp.; the parabola for H₂ gives the maximum deflexion 30 divisions in 5 seconds when the current is .22 amp.; the parabola for H₃ gives the maximum deflexion .25 division in 30 seconds, .5 in a minute when the current is .28 amp. The deflexion was very steady and sharply defined, there was none when the current was .29 amp. These figures make the ratio of permanent H₃ to the normal hydrogen as .25/180 or 1/720.

In another sample of gas the ratio was 1/480. We should expect the amount of the permanent H₃ in the gas obtained by bombardment to depend upon the length of the bombardment and the intensity of the cathode rays, and so to vary from one specimen to another.

There is a faint secondary to the H₃ parabola in fig. 2 (Pl. XXI.), indicating that part of the H₃ may be due to the short-lived H₃. The H₃ parabola is, however, so faint

compared with that for H₂ that the quantity of the permanent H₃ detected by the electrical method might well account for the greater part of its intensity.

In the photographic method the effects due to the short-lived and permanent forms of H₃ are superposed so that we cannot deduce from the ratio of the intensity of the H₃ parabola to that of the H₂ the fraction of permanent H₃ in the gas through which the discharge passes. In the electrical method the effect of the fugitive H₃ is eliminated, and the ratio of the electrical effects in H₃ and H₂ give the proportion between the permanent H₃ and the normal H₂.

Concentrated Heavy Hydrogen.

Through the kindness of Lord Rutherford I was enabled to apply the method to a specimen of heavy hydrogen in which the concentration was estimated to be about 80 per cent. The photograph of the parabolas is shown in fig. 3 (Pl. XXI.). From this we should judge that the parabolas corresponding to H₂, H₃, H₄ are of about the same intensity. In addition to these parabolas there are, as has already been observed by Zeeman, others corresponding to masses (5) and (6). The relative electrical effects due to the different lines are

$$H_1 = 11; \quad H_2 = 31; \quad H_3 = 35; \quad H_4 = 26.$$

In this case the electrical method gives for the parabolas H₂, H₃, H₄ much the same relative intensities as the photographic one, indicating that the permanent H₃ is here much more important than the short-lived. The ratio of H₄ to H₃ diminishes rapidly if the concentrated gas is diluted with a little normal hydrogen.

An interesting feature of the photograph is the occurrence in the right-hand bottom quadrant of faint parabolas corresponding to both H₁ and H₂ with negative charges; in the discharge through ordinary gases parabolas corresponding to H₁ with a negative charge are usually present, but I have seen the parabola for negative H₂ only on three or four occasions. The appearance of it in the discharge through heavy hydrogen shows that this gas can yield a particle of mass 2 with the properties of atomic hydrogen.

I am much indebted to Mr. E. Morley for the assistance he has given me in these experiments.

LXXXV. *On the Expansion of Mathieu Functions in a series of Bessel's Functions.* By S. C. DHAR, D.Sc.*

Introduction.

MATHIEU functions have been expressed in different forms, in terms of Bessel's functions, by various writers, notable amongst them being Heine †, Sieger ‡, and Dougall §. This was done also by the help of integral equations || which Mathieu functions satisfy. The object of this paper is to obtain expansions of Mathieu functions in a series of Bessel's functions by the method of successive approximations. This method had been employed by various writers ¶, notably by Profs. Whittaker and Watson **, to obtain Mathieu functions in cosine and sine forms. In this paper the same method has been utilized to obtain solutions of the first and second kind of Mathieu's equations, in a series of Bessel's Harmonics.

§ 1.

The well-known differential equation for the propagation of electromagnetic waves, reduces for the transformation

$$x+iy=h \cos h(\xi+i\eta)$$

into the form

$$\frac{d^2G}{d\eta^2} - (h^2 k^2 \cos^2 \eta - A) G = 0, \dots \dots \quad (1)$$

$$\frac{d^2F}{d\xi^2} + (h^2 k^2 \cos h^2 \xi - A) F = 0. \dots \dots \quad (2)$$

The periodic solutions of (1) in cosine or sine of multiples of η are called the *Mathieu functions*.

If we transform (1) by writing

$$\cos \eta = \mu$$

* Communicated by the Author.

† Heine, 'Kugelfunctionen,' p. 333.

‡ Sieger, *Ann. d. Phys.* xxvii.

§ Dougall, *Proc. Edin. Math. Soc.* xxxiv. pp. 191-196.

|| Dhar, *Jour. of the Dept. of Science, Cal. Univ.* ix.

¶ Dhar, *Am. Jour. of Math.* xlvi. no. 3.

** Whittaker and Watson, 'Modern Analysis,' pp. 413-415.

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and put $hk=\lambda$, we get

$$(1-\mu^2) \frac{d^2G}{d\mu^2} - \mu \frac{dG}{d\mu} - (\lambda^2\mu^2 - A)G = 0. \quad \dots \quad (3)$$

Now, again, if we put

$$\lambda\mu = z,$$

the equation (3) is again transformed into

$$(\lambda^2 - z^2) \frac{d^2G}{dz^2} - z \frac{dG}{dz} - (z^2 - A)G = 0.$$

Take

$$A = n^2 + a_n,$$

where a_n is a function of λ , such that when $\lambda \rightarrow 0$, $a_n \rightarrow 0$. The solutions of (1) in this case will reduce to $\cos n\eta$ or $\sin n\eta$, which corresponds to the Mathieu functions denoted by $ce_n(\eta)$ or $se_n(\eta)$ respectively. Hence we get for this value of A ,

$$(\lambda^2 - z^2) \frac{d^2G_n}{dz^2} - z \frac{dG_n}{dz} - (z^2 - n^2 - a_n)G_n = 0,$$

or

$$z^2 \frac{d^2G_n}{dz^2} + z \frac{dG_n}{dz} + (z^2 - n^2)G_n = \lambda^2 \frac{d^2G_n}{dz^2} + a_n G_n.$$

Denote this equation by

$$\nabla G_n = D G_n, \quad \dots \quad (4)$$

where the operators

$$\nabla \equiv z^2 \frac{d^2}{dz^2} + z \frac{d}{dz} + (z^2 - n^2) \quad \text{and} \quad D \equiv \lambda^2 \frac{d^2}{dz^2} + a_n.$$

§ 2.

If $J_m(z)$ be a Bessel's function of order m , then recurrence formula gives

$$2 \frac{d}{dz} J_m = J_{m-1} - J_{m+1}.$$

$$\therefore 2^2 \frac{d^2}{dz^2} J_m = J_{m-2} - 2J_m + J_{m+2}.$$

Hence

$$\begin{aligned} D\mathbf{J}_m &= \frac{\lambda^2}{2^2} \mathbf{J}_{m-2} + \left(a_n - \frac{\lambda^2}{2} \right) \mathbf{J}_m + \frac{\lambda^2}{2^2} \mathbf{J}_{m+2} \\ &= L\mathbf{J}_{m-2} + M\mathbf{J}_m + L\mathbf{J}_{m+2}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (5) \end{aligned}$$

and

$$\nabla \mathbf{J}_m = (m^2 - n^2) \mathbf{J}_m = \alpha_m \mathbf{J}_m, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)$$

where

$$L = \frac{\lambda^2}{2^2}, \quad M = a_n - \frac{\lambda^2}{2}, \quad \text{and} \quad \alpha_m = m^2 - n^2.$$

$$\therefore (\nabla - D)\mathbf{J}_m = -L\mathbf{J}_{m-2} - (M - \alpha_m)\mathbf{J}_m - L\mathbf{J}_{m+2}, \quad \dots \quad (7)$$

§ 3.

Solution by Continued Approximation.

Equation (3) gives us

$$\nabla \mathbf{G}_n - D\mathbf{G}_n = 0, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

A *first* approximation to (4) is a solution of

$$\nabla \mathbf{G}_n = 0,$$

which is given by \mathbf{J}_n , which we shall call \mathbf{U}_0 ,

$$\mathbf{J}_n \equiv \mathbf{U}_0.$$

If this solution be substituted in $D\mathbf{G}_n$, we get by (5)

$$L\mathbf{J}_{n-2} + M\mathbf{J}_n + L\mathbf{J}_{n+2} \equiv \mathbf{V}_1 \quad (\text{say}).$$

Write

$$\mathbf{W}_1 = \mathbf{V}_1 - \beta_1 \mathbf{J}_n, \quad \text{where } \beta_1 = M,$$

the reason for doing so is that the solution of $\nabla \mathbf{G}_n = \mathbf{J}_n$ will contain terms which will not be periodic.

A *second* approximation of (4) is given by

$$\nabla^{-1} \mathbf{W}_1 \equiv \frac{L\mathbf{J}_{n-2}}{\alpha_{n-2}} + \frac{L\mathbf{J}_{n+2}}{\alpha_{n+2}} \equiv \mathbf{U}_1 \quad (\text{say}).$$

Again, substituting \mathbf{U}_1 in $D\mathbf{G}_n$, we obtain

$$\begin{aligned} \frac{L}{\alpha_{n-2}} (L\mathbf{J}_{n-4} + M\mathbf{J}_{n-2} + L\mathbf{J}_n) \\ + \frac{L}{\alpha_{n+2}} (L\mathbf{J}_n + M\mathbf{J}_{n+2} + L\mathbf{J}_{n+4}) = \mathbf{V}_2 \quad (\text{say}). \end{aligned}$$

Write

$$W_2 = V_2 - \beta_2 J_n, \quad \text{where } \beta_2 = \frac{L^2}{\alpha_{n-2}} + \frac{L^2}{\alpha_{n+2}}.$$

A third approximation is

$$\begin{aligned} & \frac{L^2}{\alpha_{n-2}\alpha_{n+4}} J_{n-4} + \frac{LM}{\alpha_{n-2}^2} J_{n-2} \\ & + \frac{LM}{\alpha_{n+2}^2} J_{n+2} + \frac{L^2}{\alpha_{n+2}\alpha_{n+4}} J_{n+4} = U_2 \quad (\text{say}). \end{aligned}$$

Substituting U_2 in DG_n , we get

$$\begin{aligned} & \frac{L^2}{\alpha_{n-2}\alpha_{n-4}} (LJ_{n-6} + MJ_{n-4} + LJ_{n-2}) \\ & + \frac{LM}{\alpha_{n-2}^2} (LJ_{n-4} + MJ_{n-2} + LJ_n) \\ & + \frac{LM}{\alpha_{n+2}^2} (LJ_n + MJ_{n+2} + LJ_{n+4}) \\ & + \frac{L^2}{\alpha_{n+2}\alpha_{n+4}} (LJ_{n+2} + MJ_{n+4} + LJ_{n+6}) \\ & = V_3 \quad (\text{say}). \end{aligned}$$

Write

$$W_3 = V_3 - \beta_3 J_n, \quad \text{where } \beta_3 = \frac{L^2 M}{\alpha_{n-2}^2} + \frac{L^2 M}{\alpha_{n+2}^2}.$$

A fourth approximation is given by

$$\begin{aligned} & \frac{L^3}{\alpha_{n-2}\alpha_{n-4}\alpha_{n-6}} J_{n-6} + L^2 M \left(\frac{1}{\alpha_{n-2}\alpha_{n-4}^2} + \frac{1}{\alpha_{n-2}^2\alpha_{n-4}} \right) J_{n-4} \\ & + \left(\frac{L^3}{\alpha_{n-2}^2\alpha_{n-4}} + \frac{LM^2}{\alpha_{n-2}^3} \right) J_{n-2} + \left(\frac{LM^2}{\alpha_{n+2}^3} + \frac{L^3}{\alpha_{n+2}^2\alpha_{n+4}} \right) J_{n+2} \\ & + L^2 M \left(\frac{1}{\alpha_{n+2}^2\alpha_{n+4}} + \frac{1}{\alpha_{n+2}\alpha_{n+4}^2} \right) J_{n+4} + \frac{L^3}{\alpha_{n+2}\alpha_{n+4}\alpha_{n+6}} J_{n+6} \\ & \quad \text{and so on.} \quad = U_3, \end{aligned}$$

Hence equation 4) is satisfied by

$$\sum_{m=0}^{\infty} U_m,$$

provided $\sum_{m=1}^{\infty} \beta_m$ vanishes.

For

$$\nabla U_0 = 0,$$

$$\nabla U_1 = W_1,$$

$$\nabla U_2 = W_2,$$

$$\dots \dots \dots$$

$$\dots \dots \dots$$

respectively, where

$$W_m = V_m - \beta_m J_m, \quad \text{and} \quad D U_{m-1} = V_m.$$

Hence

$$\begin{aligned} \nabla \{ \Sigma U_m \} &= W_1 + W_2 + \dots \\ &= (D U_0 + D U_1 + \dots) - (\beta_1 + \beta_2 + \dots) J_m \\ &= D \Sigma U_m - J_m \Sigma \beta_m, \end{aligned}$$

or

$$(\nabla - D) \{ \Sigma U_m \} = - J_m \Sigma \beta_m.$$

$\therefore \Sigma \beta_m = 0$ will determine the constant α_n and for this value of the constant, the solution of (4) will be given by

$$G_n = \Sigma U_m.$$

It will be seen that

$$\begin{aligned} ce_n(\eta) \equiv \dots + \gamma_{n-4} J_{n-4} + \gamma_{n-2} J_{n-2} + J_n + \gamma_{n+2} J_{n+2} \\ + \gamma_{n+4} J_{n+4} \dots \infty, \quad (8) \end{aligned}$$

where

$$\gamma_{n-6} = \frac{L^6}{\alpha_{n-2} \alpha_{n-4} \alpha_{n-6}} + \dots,$$

$$\gamma_{n-4} = \frac{L^2}{\alpha_{n-2} \alpha_{n-4}} + L^2 M \left(\frac{1}{\alpha_{n-2}^2 \alpha_{n-4}^2} + \frac{1}{\alpha_{n-2}^2 \alpha_{n-4}} \right) + \dots,$$

$$\gamma_{n-4} = \frac{L}{\alpha_{n-2}} + \frac{LM}{\alpha_{n-2}^2} + \left(\frac{L^3}{\alpha_{n-2}^2 \alpha_{n-4}} + \frac{LM^2}{\alpha_{n-2}^3} \right) + \dots,$$

$$\gamma_{n+2} = \frac{L}{\alpha_{n+2}} + \frac{LM}{\alpha_{n+2}^2} + \left(\frac{L^3}{\alpha_{n+2}^2 \alpha_{n+4}} + \frac{LM^2}{\alpha_{n+2}^3} \right) + \dots,$$

$$\gamma_{n+4} = \frac{L^2}{\alpha_{n+2} \alpha_{n+4}} + L^2 M \left(\frac{1}{\alpha_{n+2}^2 \alpha_{n+4}^2} + \frac{1}{\alpha_{n+2}^2 \alpha_{n+4}} \right) + \dots,$$

$$\gamma_{n+6} = \frac{L^6}{\alpha_{n+2} \alpha_{n+4} \alpha_{n+6}} + \dots$$

Thus it is evident that for values of $\gamma_{n+2}, \gamma_{n+4}, \dots$ etc., those of $\gamma_{n-2}, \gamma_{n-1}, \dots$ etc., can be obtained.

*Calculations of the Solutions in Particular Cases.*Take $n = 0$.

Then

$$U_0 = J_0$$

and

$$DJ_0 = \left(a_n - \frac{\lambda^2}{2} \right) J_0 + \frac{\lambda^2}{2} J_2 \equiv V_1,$$

$$W_1 = V_1 - \beta_1 J_0, \quad \text{where } \beta_1 = a_n - \frac{\lambda^2}{2}.$$

Second approximation is given by

$$U_1 = \frac{\lambda^2}{2^3} J_2.$$

Further,

$$DU_1 = \frac{L}{2} (LJ_0 + MJ_2 + LJ_4) = V_2$$

and

$$W_2 = V_2 - \beta_2 J_0, \quad \text{where } \beta_2 = \frac{L^2}{2}.$$

Third approximation is given by

$$U_2 = \frac{LM}{2} \cdot \frac{1}{2^2} J_2 + \frac{L^2}{2} \cdot \frac{1}{4^2} J_4.$$

$$DU_2 = \frac{LM}{2^3} (LJ_0 + MJ_2 + LJ_4) + \frac{L^2}{2 \cdot 4^2} (LJ_2 + MJ_4 + LJ_6) = V_3,$$

$$W_3 = V_3 - \beta_3 J_0, \quad \text{where } \beta_3 = \frac{L^2 M}{2^3}.$$

Fourth approximation is given by

$$U_3 = \left(\frac{LM^2}{2 \cdot 2^4} + \frac{L^3}{2 \cdot 2^2 \cdot 4^2} \right) J_2 + L^2 M \left(\frac{1}{2 \cdot 2^2 \cdot 4^2} + \frac{1}{2 \cdot 4^2 \cdot 4^2} \right) J_4 + \frac{L^3}{2 \cdot 4^2 \cdot 6^2} J_6.$$

From this it is easy to find

$$\beta_4 = \frac{L^2 M^2}{2 \cdot 2^4} + \frac{L^4}{2 \cdot 2^2 \cdot 4^2}.$$

Hence $\sum \beta_m = 0$ gives

$$* a_n = \frac{\lambda^2}{2} - \frac{\lambda^4}{2^5} + \frac{7}{2^{15}} \lambda^8, \dots \quad (9)$$

and the solution (up to the 6th power of λ) is

$$\begin{aligned} J_0 + \left(\frac{1}{2^3} \lambda^2 - \frac{7}{2^{13}} \lambda^6 + \dots \right) J_2 - \left(\frac{1}{2^9} \lambda^4 + \dots \right) J_4 \\ + \left(\frac{1}{2^{13} \cdot 3^2} \lambda^6 + \dots \right) J_6 + \dots \quad (10) \end{aligned}$$

It will be seen that this represents the expansion of $ce_0(\eta)$ in a series of Bessel's functions.

§ 5.

The expansions of $ce_1(\eta)$ and $ce_2(\eta)$ have also been obtained, with the corresponding values of a_n . They are given below :—

$$(i.) \text{ When } a_n = \frac{3}{2^2} \lambda^2 - \frac{1}{2^7} \lambda^4 - \frac{1}{2^{12}} \lambda^6,$$

$ce_1(\eta)$ is given by

$$\begin{aligned} J_1 + \left(\frac{1}{2^5} \lambda^2 + \frac{1}{2^{10}} \lambda^4 + \frac{1}{3 \cdot 2^{15}} \lambda^6 + \dots \right) J_3 \\ + \left(\frac{1}{3 \cdot 2^{10}} \lambda^4 + \frac{1}{3^2 \cdot 2^{13}} \lambda^6 + \dots \right) J_5 \\ + \left(\frac{1}{3^2 \cdot 2^{15}} \lambda^6 + \dots \right) J_7 + \dots \quad (11) \end{aligned}$$

$$(ii.) \text{ When } a_n = \frac{1}{2} \lambda^2 + \frac{5}{3 \cdot 2^6} \lambda^4,$$

$ce_2(\eta)$ is given by

$$\begin{aligned} \left(-\frac{1}{2^4} \lambda^2 + \frac{5}{3 \cdot 2^{12}} \lambda^6 + \dots \right) J_0 + J_2 \\ + \left(\frac{1}{3 \cdot 2^4} \lambda^2 + \frac{43}{3^3 \cdot 2^{15}} \lambda^6 + \dots \right) J_4 \\ + \left(\frac{1}{3 \cdot 2^{11}} \lambda^4 + \dots \right) J_6 \\ + \left(\frac{1}{2^{15} \cdot 3^2 \cdot 5} \lambda^6 + \dots \right) J_8 + \dots \quad (12) \end{aligned}$$

* It will be seen that (9) reduces to the form given in (1) Ex. 2 of 'Modern Analysis,' by Whittaker and Watson, on writing

$$a_n = a + \frac{\lambda^2}{2} \quad \text{and} \quad \lambda^2 = -32q.$$

§ 6.

Again, if in the differential equation (1) we put

$$kh=i\lambda \quad \text{and} \quad \sin \eta = \mu$$

it is transformed into

$$(1-\mu^2) \frac{d^2G}{d\mu^2} - \mu \frac{dG}{d\mu} + \lambda^2(1-\mu^2)G + AG = 0,$$

which reduces to, on transformation by the relation $\lambda\mu = z$,

$$\begin{aligned} z^2 \frac{d^2G_n}{dz^2} + z \frac{dG_n}{dz} + (z^2 - n^2)G_n &= \lambda^2 \frac{d^2G_n}{dz^2} + (\lambda^2 + a_n)G_n, \\ &= \lambda^2 \frac{d^2G_n}{dz^2} + a_n'G_n, \quad a_n' = a_n + \lambda^2, \end{aligned}$$

i. e., $\nabla G_n = DG_n$ (13)

The method of solving this is the same as that given in previous articles, with only this difference, that in (8) we

shall have to substitute $a_n + \frac{\lambda^2}{2}$ in place of $a_n - \frac{\lambda^2}{2}$. It

will be seen that these will give Mathieu functions represented generally by $se_n(\eta)$. It is needless to proceed to their construction, as they can be easily written down from those already given.

Again, as Bessel's functions of the second kind, Y_n (say Hankel's form), satisfies the same recurrence formulæ as J_n , it is evident that if, in place of J_n , Y_n be substituted in (8), we will get solutions of second kind of Mathieu's equation, in Bessel's functions.

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LXXXVI. *A Determination of the Radium-Content of some South African Granites. By M. N. S. IMMELMAN, M.Sc. (Cape Town), Lecturer in Physics at the University of Pretoria **.

AS pointed out by Joly † in 1911, the old solution method used for determining the radium-content of rocks was very slow and tedious and left much to be

* Communicated by the Author.

† Joly, Phil. Mag. ix. p. 134 (1911).

desired in the way of accuracy. Bringing the rock into complete solution is a very difficult process ; in some cases the rock has to be fused several times with the carbonates of sodium and potassium, and even then it is doubtful whether there is complete solution. So much handling of the rock naturally leads to a greater risk of contamination, and the results cannot be relied upon.

The furnace method described by Joly in the same paper is a great improvement on the solution method, and it seems to be the only way of getting reliable results.

In the present determination a new form of furnace was used. This was found to be very satisfactory, and a description of the furnace may be of interest to others working in the same field.

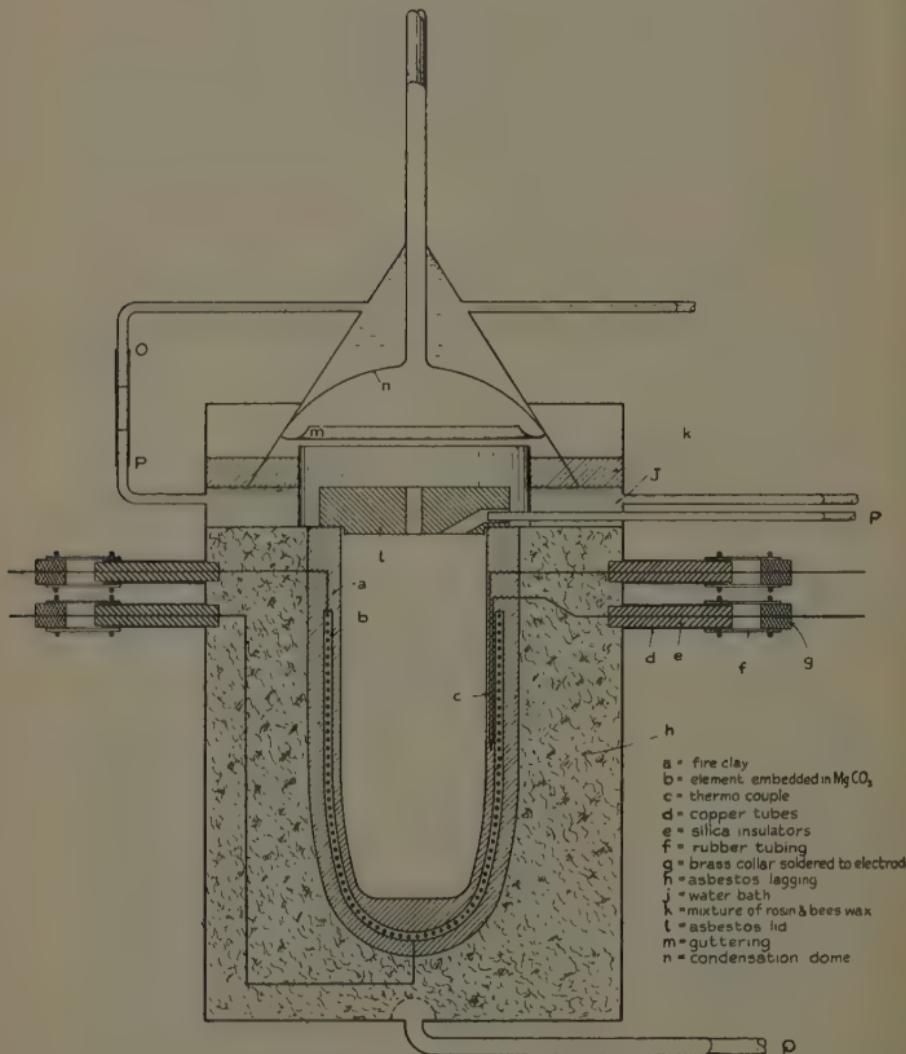
The heating element was constructed as follows :— A wooden former was made of the same shape as the crucible to be used in the furnace but only slightly larger. On the one side a flat strip of wood $\frac{1}{2}'' \times \frac{1}{16}''$ was nailed ; this makes provision for the insertion of the thermocouple afterwards.

A mixture of fireclay and asbestos wool was made into a thick paste with water ; a thin layer of this paste was put round the former and baked semi-hard in a flame. Some magnesium carbonate powder was also made into a thick paste with water, and a layer about $\frac{1}{8}''$ thick of this was put round the fireclay asbestos. When this also had been made semi-hard in a flame, some iron tacks were driven through it into the hemispherical base of the wooden former, and with the help of these tacks the heating wire was wound outwards in a spiral, from the lowest point, till the hemispherical portion had been passed. After this the winding was continued around the cylindrical wall of the wooden former. About 20 grm. of 30 S.W.G. platinum wire, taken double, was used. The wire was pulled fairly tight so as to be embedded in the carbonate. Round the outside of the wire another layer of magnesium carbonate paste was put and baked hard. The tacks were then withdrawn, and a thick layer of the asbestos-fireclay paste was put round the outside of the magnesium carbonate to keep it firmly in place.

After passing a current through the wire to drive out all the water and bake the fireclay and carbonate hard the wooden former could easily be removed.

One end of a platinum-nickel-chrome thermocouple was now cemented with fireclay paste into the groove left on the inside of what will from now on be called the "element."

Fig. 1.



The furnace as described in this paper.

The element was next packed in asbestos wool in a two-litre copper calorimeter. In the side of the calorimeter and near the top edge four pieces of $\frac{1}{4}$ " brass tubing, each

about 3" long, were soldered. A similar piece of tubing was silver-soldered into the bottom of the calorimeter.

From fig. 1 it is clear how air-tight connexions were made between the lead-in wires and the wires of the element and thermocouple respectively.

The top of the furnace was now closed in as shown in the figure. The asbestos lid *l* has a sloping groove which fits over the end of the air inlet tube *p*. When air is let into the furnace it is diverted down into the crucible by the groove, and so ensures that all gases collected in the crucible are effectively swept out. The lower inlet *q* allows a thorough sweep-out of all gases which have escaped through the lid and have collected in the asbestos-wool lagging.

When the furnace is to be used the wax *k* on top of the water-cooling-bath is melted by playing on it with a flame, and when quite soft the brass funnel shown is inverted over the top, pushed down into the wax, and the rubber tubing *OP* slipped on. If, now, a fast stream of cold water is circulated through the water-cooling-bath, the wax sets hard and holds the funnel down firmly, making the whole furnace absolutely gas-tight.

The funnel being kept cold by circulating water acts as a condenser. The dome shape of the inside of the funnel allows any condensed water to flow down into the continuous circular gutter which is soldered round the inside of the funnel, thus preventing the water from collecting on the wax.

The thermocouple used was a platinum-nickel-chrome couple; this proved very satisfactory, for temperatures from 500° C. to 1200° C. the E.M.F.-temperature curve is practically a straight line. The metals are easily joined by fusing them together in an oxy-coal gas flame. The current required to bring the temperature of the furnace up to 1100° C. is about 5 amperes.

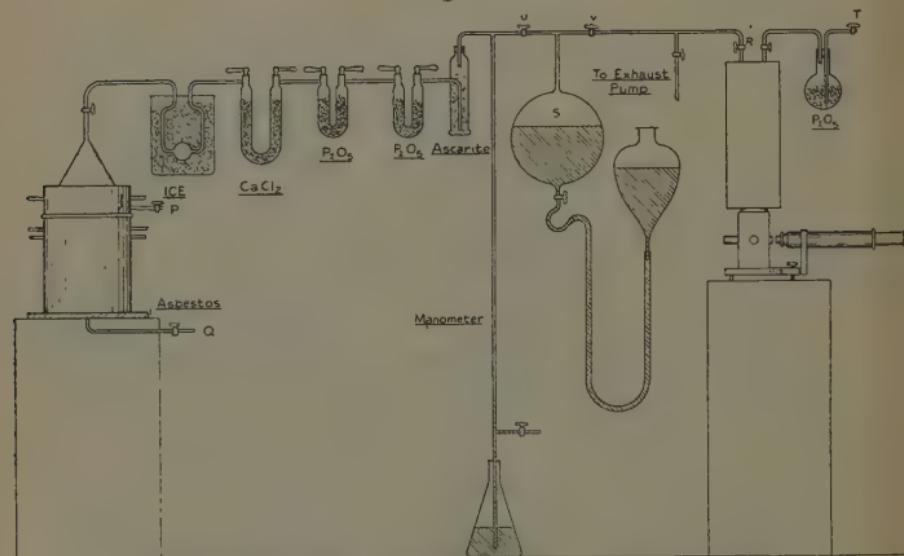
Determination of the Radium-content of Rocks.

Fig. 2 shows the arrangement of the apparatus as used in the present set of experiments. The rock was finely ground to pass a sieve of 80 mesh to the inch. Six grm. of this rock powder was then mixed with about 18 grm. of the mixed carbonates of sodium and potassium. This mixture was then put into a small platinum crucible and

the crucible carefully lowered into the furnace. With the lid (*l*) in place the funnel is sealed on and a fast stream of cold water passed through the funnel and water bath.

After adjusting the mercury level in the receiver (*s*) so that the volume of the space above is slightly less than the volume of the electroscope the whole apparatus is exhausted, the tap (*R*) leading to the electroscope being left closed. The tap *V* is now closed. With the tap *T* open the electroscope is left open to the atmosphere and hence its natural leak can be determined while the furnace is heating up, the gases coming from the furnace meanwhile collecting in *S*.

Fig. 2.



General arrangement of apparatus used in these experiments.

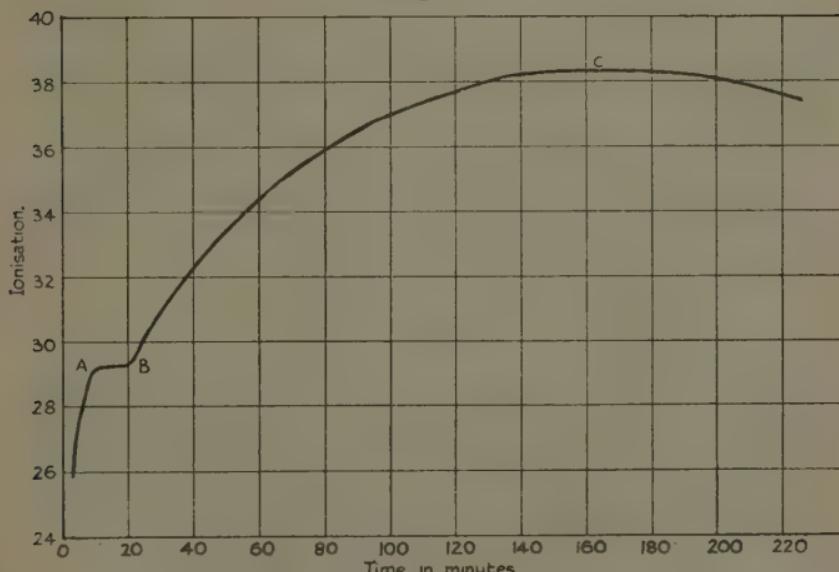
After the gases have gone through the drying-tubes they are passed through a tube containing a NaOH-asbestos compound known as Ascarite. The ascarite removes practically all the carbon-dioxide; the pressure rises very little during the whole fusion, and hence a thorough washout of the furnace is obtained at the end.

When the temperature of the furnace is at about 1100°C . it is kept there for about 15 minutes and then both taps *P* and *Q* are opened and the furnace is swept out very completely. The taps *U* and *V* are now closed

and the gases left in S long enough for any thorium emanation which might have come over to decay. Meanwhile the electroscope is exhausted, the pump is shut off, R and V are opened, and the gases from S pushed over into the electroscope by raising the mercury level in S. If, now, U is opened a final washout is obtained and the electroscope brought to atmospheric pressure.

For the radium emanation in the electroscope to get into equilibrium with its decay products takes about three hours, and when working with rocks of low radium-content it is best to time the electroscope after this

Fig. 3.



Decay curve for Ra emanation.

equilibrium has been established, as then the ionization produced is a maximum. In dealing with rocks of fair radium-content as, for example, the granites here analysed, it saves time if one makes use of the temporary equilibrium stage observed in the decay curve of radium emanation.

It will be noted that after about 10 minutes the rate of decay remains constant for 10 minutes between the points A and B. After this the rate goes up, until after about 5 hours it begins to fall with the half-value period of radium emanation itself. From the curve it will be

seen that at C the ionization is 30 per cent. more than at AB. In the experiment, then, the electroscope is timed over the flat portion AB and the result multiplied by 13/10, which gives the maximum rate at C. Apart from saving time this also reduces the amount of radioactive matter deposited on the inside of the electroscope, the emanation being kept inside the electroscope only for about 20 minutes *.

While the electroscope is timed the furnace is opened and allowed to cool before the next charge is introduced.

The constant of the electroscope was determined in three different ways :—

(a) A standard solution of radium, which had been left sealed up for four weeks in a curie vessel was boiled, air was then bubbled through the boiling solution and passed through drying-tubes into the exhausted electroscope. With the electroscope at atmospheric pressure the rate of collapse of the leaf was carefully determined. Knowing the amount of radium in the standard solution and the rate of collapse caused by the emanation in equilibrium with it the constant can be calculated.

(b) A known weight of carnotite was brought into solution by dissolving it in nitric acid. This solution was diluted down until 30 c.c. of solution contained approximately the same amount of radium as the standard solution, assuming the carnotite to contain 65 per cent. uranium. In this way the radium-content of the carnotite was accurately found. 15 milligram. of this carnotite was now well powdered and mixed with 30 grm. borax glass. This was then fused and finely ground up in an agate mortar. About 100 milligrm. of this powder was mixed with 6 grm. of rock powder for which the rate of leak produced in the electroscope had been previously determined by fusion with mixed carbonates. When this mixture of rock and carnotite is fused in the ordinary way with mixed carbonates, then the increase in the rate of leak produced by the known amount of radium in the carnotite can be found, and hence the constant of the electroscope determined under the same conditions as hold in an ordinary experiment †.

(c) As a check a rock very kindly sent me by Professor Joly was analysed and its radium-content

* Satterly, *Phil. Mag.* **xx.** (1910).

† J. H. J. Poole and J. Joly, *Phil. Mag.*, **xlviii.** p. 820 (1924).

calculated, using the constant as found by (a) and (b). The value found agreed with that given by Professor Joly to within about $2\frac{1}{2}$ per cent.

The constant used throughout these experiments was the mean of those obtained by methods (a) and (b), viz., $1 \cdot 10 \times 10^{-12}$ grm. radium for a rate of leak of one scale division per hour.

The rate of leak could be measured very accurately, as a very fine quartz fibre was attached to the leaf of the electroscope. The natural leak of the electroscope was very small, for it was practically constant at 3.5 divisions per hour; it was, however, determined before each experiment.

The carbonates were mixed in large quantities and for each quantity a blank experiment was done to make sure that there was no leak caused by the carbonates themselves. Before starting the day's experiments it was found advisable to run a blank experiment to drive off any emanation that may have collected in the furnace due to contamination.

Typical Experiment.—Sample No. 13.

7 grm. rock powder mixed with 22 grm. mixed carbonates.

Gases collected into receiver S by 3.50 P.M.

Gases collected into electroscope by 4.05 P.M.

Leak observed from 4.18 to 4.34 = 15.40 divs. per hour.

Corrected for natural leak this becomes = 11.9 divs. per hour.

Maximum leak after 3 hours = $\frac{11.9 \times 13}{10} = 15.47$ divs. per hour.

Electroscope constant = $1 \cdot 10 \times 10^{-12}$ grm. Ra for a leak of 1 div. per hour.

Radium-content of rock = $\frac{15.47 \times 1 \cdot 10 \times 10^{-12}}{7}$ grm.

Ra per grm. rock.

Radium-content of rock = 2.43×10^{-12} grm. Ra per grm. rock.

Several experiments were done with this sample, but in each case the rock was ground to a different degree of fineness; but from the results obtained it appeared that the results were not affected by the degree of fineness.

within fairly wide limits. The values obtained for four determinations were in order of fineness: 2.68×10^{-12} , 2.70×10^{-12} , 2.43×10^{-12} , and 2.52×10^{-12} .

The following results were obtained for samples of Nama Granites kindly given to me by Dr. D. Scholtz of the Department of Geology of the University of Pretoria. The samples were collected in the South Western districts of the Cape Province. The values given are the mean of several determinations:—

Sample no.	Class of granite.	Locality.	Radium-content per grm. in grm. $\times 10^{-12}$.
2	Coarse porphyritic.	Saldana.	2.40
3	Granite porphyry.	Saldana;	3.47
4	Coarse porphyritic.	Mamry Station.	3.24
5	Mafic fine even-grained.	Doornfontein, Darling.	2.24
6	Mafic fine even-grained.	Klaver Vlei, Darling.	3.02
7	Coarse porphyritic.	Diep River, Malmesbury.	3.06
8	Fine granite facies.	Paardeberg, Malmesbury.	2.19
11	Quartz porphyry.	Paarl Diamant, Paarl.	1.61
13	Coarse porphyritic.	Kloof Nek, Cape Town.	2.60
12	Coarse porphyritic.	Tin Mines, Kuils River.	3.38
14	Coarse even-grained.	Railway-cutting, Sir Lowries Pass.	2.82
16	Porphyritic.	Trigonometrical Beacon Robertson.	2.83
17	Granite.	Bruintjies River, Swellendam.	1.92
18	Even-grained.	Wilderness, George.	2.41
19	Diorite.	Ysterfontein, Darling.	2.62
20	Poikilitic diorite.	Ysterfontein, Darling.	1.50
21	Melanocratic inclusions in poikilitic diorite.	Ysterfontein, Darling.	1.1
22	Veins traversing poikilitic diorite.	Ysterfontein, Darling.	1.86

In conclusion, I wish to thank the Research Grant Board and the authorities of this University for their financial assistance which made this work possible. I also wish to thank Dr. D. Scholtz for kindly supplying me with the samples.

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University of Pretoria,
Pretoria, South Africa.

LXXXVII. *Colorimetry with a Spectrometer.* By R. A. HOUSTOUN, *D.Sc., F.Inst.P., Lecturer on Physical Optics in the University of Glasgow* *.

Introductory.

IF a very accurate determination of an electrical resistance were required, probably the best procedure would be to send it to the National Physical Laboratory. But a good determination could be obtained from nearly any college or science school in the country. No matter what the demands for teaching are, there is always some apparatus kept in good condition, and the methods of measuring a resistance are well understood. It is, however, quite different with the measurement of colour, and yet colour touches human experience more closely than electrical resistance. A scientific method of measuring colour was established by the Commission Internationale de l'Eclairage held at Cambridge in 1931, and it is in use at the N.P.L., but there are very few laboratories in the country which can apply it, or are, indeed, interested in the matter. One reason for this is that there is no simple apparatus for the measurement of colour which is based on the theory of colour. In 'Colour and Methods of Colour Reproduction' L. C. Martin emphasizes the need for such an apparatus †, stating that it should be simple, inexpensive, and easily made all over the world, and there is general agreement with him. I would add to the specification, that a science school teacher should be able to understand and operate the apparatus without too much trouble, and that inaccuracy should be detected automatically. The need

* Communicated by the Author.

† P. 29, London, 1923.

for such an apparatus is urgent, for unless the international colour coordinates can be measured by the average physicist, there is little chance of their general adoption.

I have devised several simple colorimeters *. These instruments have all been successful up to a point, but after using them I have felt I could do better. In the footnote to the last paper referred to I indicated that a further method was being tried. It in itself was not too satisfactory, but it led to the method to be described in the present paper. This fulfils all my requirements, and is a great advance on anything I have used hitherto.

The Apparatus.

The method employs a spectrometer, W. Wilson's well-known No. 1 College Spectrometer. The slit opens symmetrically, the circle reads to 30", and the lenses of telescope and collimator have a focal length of about ten inches and a clear aperture of about one inch. The prism is of Iceland spar and is cut with its refracting edge parallel to the optic axis. The angle is $60^\circ 20\cdot6'$. The faces are nearly square and of edge about six-tenths of an inch in length. The direction of the optic axis must be nearly right, because, when the refractive index for Na light was determined by the method of minimum deviation, the result was accurate in both cases to the fourth decimal place.

An Iceland spar prism of this nature forms two spectra, the less deviated one being plane polarized in a horizontal plane and the more deviated one being plane polarized in a vertical plane. These are separated by a dark space. Only the more deviated spectrum is used, and the prism was set so that the Na line of this spectrum was at minimum deviation. The following table then gives the data for the calibration of this spectrum :—

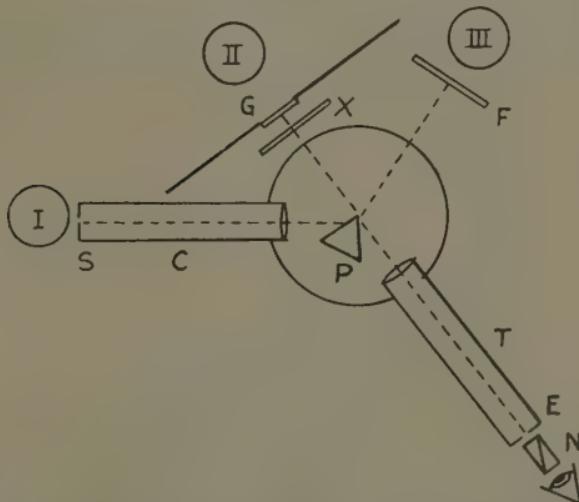
Na	5893 Å. $80^\circ 6'$	He	5016 Å. $80^\circ 53\frac{3}{4}$
Tl	5351 Å. $80^\circ 33'$	He	4922 Å. $81^\circ 1'$
He	7065 Å. $79^\circ 27'$	He	4713 Å. $81^\circ 18'$
He	6678 Å. $79^\circ 37'$	He	4471 Å. $81^\circ 41'$
He	5876 Å. $80^\circ 6\frac{1}{2}'$		

The eyepiece was replaced by a slit E (fig. 1), in front of which rotated a nicol N with square ends.

* Proc. Int. Congress of Photography, 1928, p. 431; Trans. Opt. Soc. xxxiii. p. 199 (1931-32); Phil. Mag. xvi. p. 945 (1933).

III is an opal Osram lamp in front of which is placed a red, blue, magenta, or other filter. This lamp is seen by reflexion on the second face of the prism. Moreover, its light is incident on the surface within 2° of the polarization angle, so that it is almost completely plane polarized by reflexion in the horizontal plane. The eye looking through the slit at E sees the second face of the prism illuminated uniformly by one of the colours of the spectrum, for example, green. Superposed on this is the image of the lamp III, coloured, for example, a uniform red. This image covers the whole surface of the prism. As the

Fig. 1.

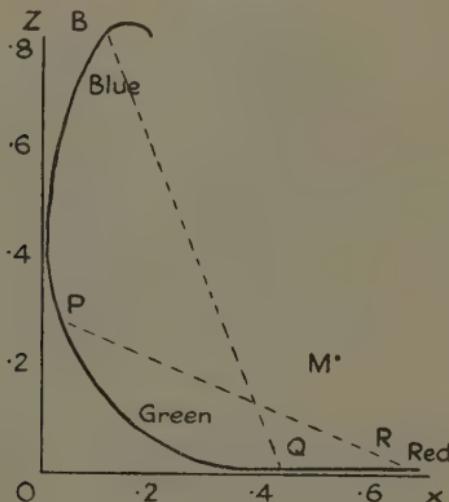


two colours are plane polarized at right angles to each other, their relative proportion in the mixture can be altered by rotating the Nicol. Thus the colour of the face of the prism can be changed gradually from red to green.

Let us consider the matter from the standpoint of the colour diagram. Every colour has three coordinates, x, y, z , but as $x+y+z=1$ always, one of these is superfluous. It is most convenient to use x and z , as the spectrum then lies roughly along the coordinate axes. Fig. 2 shows its position on this basis. The colour of the opal lamp, as seen through the red filter, is represented by the point R. Let P be the spectrum colour on which it is superposed. Now it is the property of the diagram that, when the proportions of two superposed colours are altered, the

point representing their mixture travels along the straight line from the one colour to the other. Thus in the case of the red filter and the green spectrum colour the mixture moves along the straight line PR. But by rotating the telescope different spectrum colours can be brought in succession on to the face of the prism, and the image of the opal lamp is large enough not to move off the face of the prism. So in this way the whole area of the diagram can be covered with the exception of the small part lying to the right of the line joining R to the violet end of the spectrum.

Fig. 2.



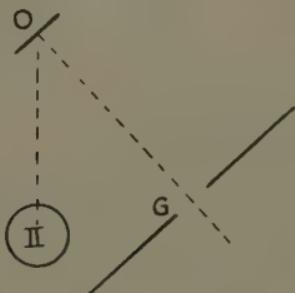
Now suppose that the red filter is replaced by the blue one, represented by the point B. The blue light can then be superposed on any colour of the spectrum, and when the nicol is rotated, the colour of the face of the prism travels along some such line as BQ. In this way the area of the diagram can be covered a second time. The position of the magenta filter is approximately given by M, and by its use the area of the diagram can be covered a third time.

Fig. 1 is a plan of the apparatus as arranged for measuring the colour of a piece of coloured glass X. G is a large screen with a window in it covered with matt glass; the latter was illuminated by a Pearl Osram lamp, II. The intensity of this illumination could be regulated by

altering the distance of II from the matt glass. The eye looking through E saw X beyond the edge of the prism. The line of separation between X and the face of the prism was a very sharp one ; I had no idea it was possible to put such a sharp edge on an Iceland spar prism. The lamp I in front of the slit was also a Pearl Osram ; I, II, and III were all 220 volt 40 watt lamps, but they were operated at 250 volts for the sake of the extra brightness. They were, of course, all enclosed, so as to keep the room in darkness.

The red filter was a piece of red signal glass. It matched 6275 Å. on the spectrum, the coordinates of which are $x=704$, $z=0$. The blue was the Wratten standard tricolour, No. 76 ; it matched 4770 Å., the coordinates of which are $x=103$, $z=794$. The magenta was the Wratten standard complementary, No. 32.

Fig. 3.



The eye slit E was about 0.4 mm. wide and consequently subtended about 5' at the prism. If it was reduced below this value definition was impaired. The slit S was kept at a constant value somewhat less than this, and the intensities of the two halves of the field were matched by moving the lamp II.

The purity of the spectrum was tested by inserting narrow region filters in front of the slit, but this had no effect on the settings. There was a little trouble at first owing to white light escaping over the top of the filter F and being scattered by the back surface of the Iceland spar prism, which was at first matt. But this was got over by stopping the leak and polishing the surface and made only a difference of 1' in one of the settings.

When the colour of an opaque surface O is measured (fig. 3), the matt glass is removed from the screen G, the

surface is placed so as to be viewed normally, and the lamp II illuminates it at 45° .

When viewed through the eyepiece slit the breadth of the face of the prism was rather more than half its height. The prism was about 12 inches from the eye-slit, so the breadth subtended an angle of about $1\frac{1}{2}^\circ$ and the height about 3° at this point.

The First Measurements made.

The first measurement made with the apparatus was a determination of the colour of lamp II. The red filter was placed at F, and the telescope and nicol adjusted until the colour of the prism face was the same as that of the matt glass at G. Lamp II was then shifted until the intensities of the comparison fields were the same, and the telescope and nicol adjusted again. The matching of intensities was not necessary, but it made the telescope setting more accurate. The match took place at a point in the blue-green. The wave-length of this point was read from the calibration curve, its coordinates x and z obtained from the table given by Smith and Guild *, and the point entered in the diagram and joined to the point representing the red filter (*cf.* fig. 4). A number of copies of the diagram were made by the opalograph in order to facilitate working.

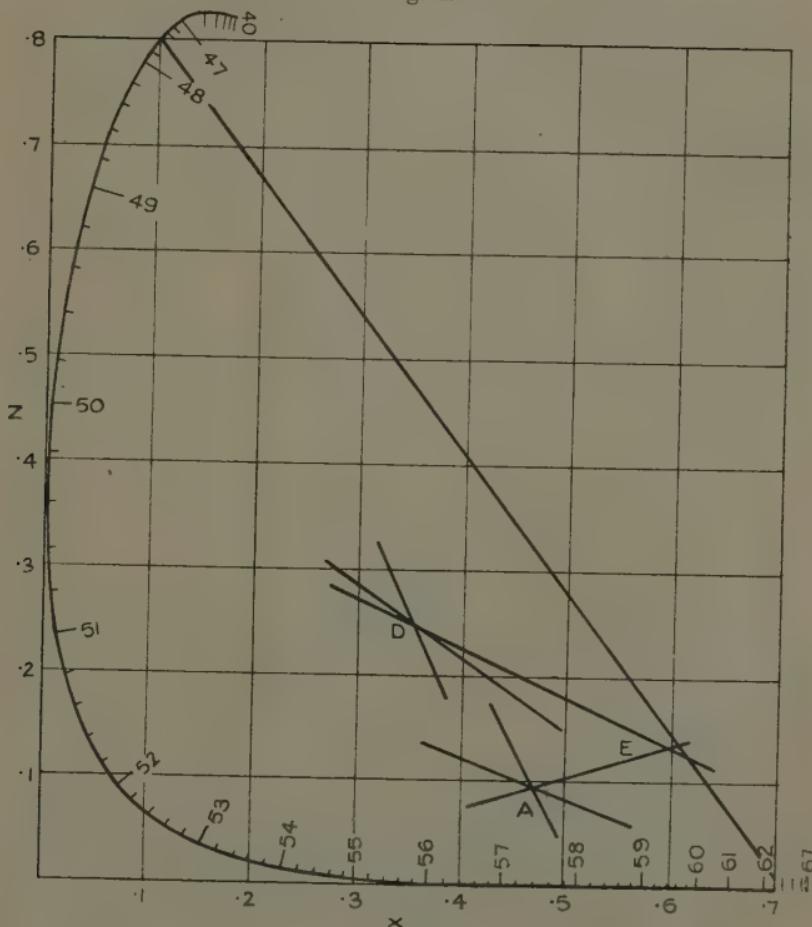
The blue filter was then placed at F, and the telescope, nicol, and lamp II adjusted until the colours matched again. This happened at a point in the yellow of the spectrum. This point was joined to the position of the blue filter, and the intersection of the two lines gave A, the colour of lamp II. The magenta filter was then placed in position at F and a colour match obtained again, this time at a point in the green. A line AE was drawn through this point and A. It gave the direction of magenta.

A Wratten "tungsten to daylight" filter, No. 78, was then placed in position at X, and a match obtained in succession with the red, blue, and magenta filters. The results are shown in the same diagram, D giving the colour of the daylight filter and DE the direction of magenta. The intersection of AE and DE gives E, the colour of magenta.

* T. Smith and J. Guild, "The C.I.E. Colorimetric Standards and their Use," *Trans. Soc.* xxxiii. p. 73 (1931-32).

As a check on the result the magenta filter was placed at X and the red filter at F. A match was obtained when the telescope was turned to a point in the blue extremely close to the position of the blue filter. This point was joined to the position of the red filter and the straight line almost passed through E. The degree of coincidence

Fig. 4.



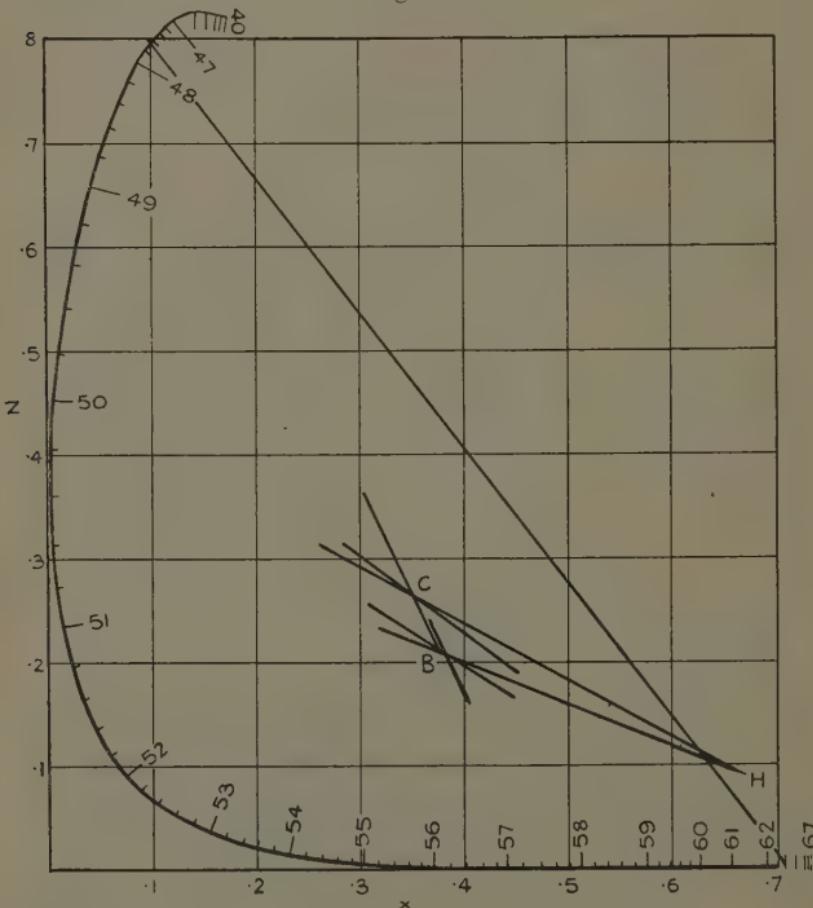
A, tungsten lamp ; D, same with daylight filter ; E, magenta.

gives a measure of the accuracy of the observations. It should be noted that we assume here that lamps II and III have the same colour temperature.

The Commission Internationale sanctioned the use of three standard illuminants, a gas-filled lamp operated at 2848° K. and the same lamp in combination with liquid

filters to yield sources of colour temperature of about 4800° K. and 6500° K. In Resolution (2) of the Commission these standards are referred to as A, B, and C. I made the assumption that my lamp II had the colour of standard A, and had the filters made up for giving

Fig. 5.



B and C, standard illuminants; H, magenta.

B and C. These filters were placed in succession at X (fig. 2), and their colours determined in succession with the red, blue, and magenta filters at F. The results are shown in fig. 5, B and C giving the positions of the standards denoted by the same letters. The point H gives magenta, and the degree of concurrency here again gives an idea of the accuracy of the work. Each of the

positions shown in figs. 4 and 5 is the mean of two careful settings.

In figs. 4 and 5 we have altogether five lines passing through magenta. Of these the line from red to blue is undoubtedly the most accurate. Its intersections with the other four are given by (·608, ·132), (·613, ·128), (·624, ·109), and (·622, ·120) giving a mean of $x=·617$ and $z=·122$. The positions of the points A, B, and C on my diagrams are, however, not satisfactory. The xz co-ordinates of these points are given by Smith and Guild (*loc. cit.* p. 106) as (·448, ·145), (·348, ·300), and (·310, ·374), so that the A, B, and C on my diagrams are all considerably to the red side of their correct positions. I do not know to what the discrepancy is due—possibly the assumption that my lamp II was giving a colour temperature of 2848°K , or possibly to the matt glass G absorbing selectively. I have no method of measuring colour-temperature at my disposal except by means of a spectro-photometric comparison with the Hefner lamp, and this is not an accurate method, but according to it the colour temperature of lamp II is not far off the correct value. The explanation of the discrepancy is being reserved for future investigation *.

Discussion of the Method.

The graphical method of finding the position of a point on the colour diagram was used by Dow and myself in 1923 † and by J. Guild in 1925 ‡. Guild refers to it as the method of vector colorimetry and has constructed an apparatus for applying it. This consists essentially of a constant deviation spectrometer with two parallel collimators, before the slits of which are fitted absorbing wedges for regulating the intensities of the beams, and a Lummer Brodhn photometric cube on which the light falls after issuing from the telescope. It is thus an apparatus of a very special nature, and it does not appear to have been used for any investigation. Guild's paper contains some interesting remarks on the scope of the method, chief of which is the statement that it "is one of the most fool-proof methods available for the measure-

* The discrepancy is due to the differences between observers of normal colour-vision being greater than I anticipated.

† *Phil. Mag.* **xlv.** p. 169 (1923).

‡ *Trans. Opt. Soc.* **xxvii.** p. 139 (1925-26).

ment of colour quality." I certainly agree with this: by using different filters in front of lamp III one can get a number of lines through the point, and inaccurate work will at once be detected.

But the method has other advantages. It works directly to the coordinates x , z , without having to make a detour through the working primaries of a trichromatic colorimeter. There is a pleasure in drawing the lines and seeing exactly on paper what part of the field one has been sweeping over. Also the fact that the relative intensity of the two superposed beams is not measured, is a great advantage from the standpoint of the occasional user, because the distinction between the "quantity" of a beam in the colour mixing sense and its luminosity is difficult to appreciate, and, unless the experimenter has time to go into the matter thoroughly, it is better to employ a method which evades the difficulty altogether.

It will be noted that, except for the Iceland spar prism, the arrangement contains nothing that should not be part of the equipment of any good laboratory. If the laboratory does not possess a spectrometer with a nicol eyepiece, there is every probability that it may possess some old polarimeter nicol that can be adapted for the purpose. A nicol eyepiece can be used for many other purposes, so with my arrangement scientific colorimetry is no longer a measurement requiring special apparatus of an expensive nature, but is only one of the uses of the polarization spectrometer.

It will be noted that the eyepiece nicol does not require a graduated circle. It is also not necessary that the collimator slit should open symmetrically. I at first used this slit as a means of regulating the intensity of the spectrum, but came finally to the conclusion that it was better to use the same slit width for all measurements. The only reading taken is that of the telescope vernier; this has, however, to be taken very carefully. It would be an advantage if the dispersion of the prism were greater, but it is simpler to use one equilateral spar prism than to have a glass prism and a spar prism in series, and it seems right to explore the possibilities of the simpler arrangement first.

In order to get a line on highly saturated colours I have used a green filter, Wratten No. 74, which coincides with 5360 Å. In order to measure purples and pinks two

reference points are required in this region of the diagram. The magenta filter I have used and one between it and the violet end of the spectrum would do excellently. While the positions of these can be obtained from the apparatus itself, each determination involves the cumulative error of four settings of the telescope, and it would be an advantage, if such filters could be obtained with their colour coordinates certificated.

It would also be of considerable help to experimental work in this field, if some one would publish a table giving the colour coordinates and black body temperature of a well-known make of gas-filled lamp for different currents and efficiencies.

The Colour Coordinates.

The colour coordinates have been published in tabular form to four significant figures for every 1 m μ from 380 m μ to 700 m μ by Smith and Guild (*loc. cit.*) and by Deane B. Judd *. As the Trans. of the Opt. Soc. and the J. O. S. A. are not accessible to the average physicist, an extract from the tables is given here :

m μ .	x.	z.	m μ .	x.	z.	m μ .	x.	z.
400173	.822	504004	.363	560373	.002
460144	.826	506005	.319	565409	.002
470124	.818	508008	.276	570444	.001
475110	.804	510014	.236	575479	.001
480091	.776	512022	.198	580512	.001
482083	.760	514033	.164	585545	.001
484073	.741	516045	.135	590575	.001
486064	.718	518059	.111	595603	.001
488055	.691	520074	.092	600627	.000
490045	.660	525114	.060	610666	.000
492036	.624	530155	.039	620691	.000
494027	.584	535193	.025	630708	.000
496020	.542	540230	.016	640719	.000
498013	.498	545266	.010	670732	.000
500008	.453	550302	.006			
502005	.408	555337	.004			

* Deane B. Judd, "The 1931 I.C.I. Standard Observer and Coordinate System for Colorimetry," *Journal of the Optical Society of America*, xxiii. pp. 359-374 (1933).

LXXXVIII. *The Madelung Constants for some Cubic Lattices.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN a note published in the Philosophical Magazine for November 1932, Dr. Sherman stated that my value for the Madelung constant for cuprite is incorrect, because in deducing this value from the fluorite constant I had omitted to allow for the difference between twice the potential of the oxygen ions with respect to a copper ion at $\frac{11}{44}$ and that of the fluorine ions with respect to half a calcium ion at the centre of one of the cubes.

I have corresponded with Dr. Sherman, who, on February 2nd, 1933, wrote to say that he agrees with my contention that there is no difference between these two potentials, that the reason he gave for the discrepancy between my result and Emersleben's was invalid, and that, although he feels certain my result is incorrect, he is unable to point out just where my mistake may be.

I have delayed writing as I understood Dr. Sherman intended a year ago to publish a further note on the subject.

Yours faithfully,
T. S. WHEELER.

Royal Institute of Science,
Bombay.
28th February, 1934.

LXXXIX. *Experiments on the Polarization of Electrons.*

By G. P. THOMSON, M.A., F.R.S., Professor of Physics at the Imperial College of Science and Technology *.

Introduction.

IT is well known that in order to explain optical spectra it is necessary to assume that an electron has more than the three degrees of freedom associated with a point. In the usual model it is regarded as a spinning body with magnetic moment $eh/4\pi mc$ and mechanical moment $h/4\pi$. There is nothing in the de-Broglie-Schrodinger wave

* Communicated by the Author.

mechanics corresponding to this, and the theory is thus unable to account for effects like the fine structure of the hydrogen spectrum or to predict correctly the results of the Stern-Gerlach experiment.

In Dirac's relativistic wave theory this defect is removed, and the electron appears with directional properties resembling those of the spinning model. Darwin, who has extended Dirac's theory and expressed it in a more geometrical form, shows that, for speeds small compared with that of light, a freely moving electron has a magnetic moment $eh/4\pi mc$. The direction of the magnetic axis has no necessary relation to the direction of motion of the electron and need not be in the wave front, nor can it be determined by measuring the force which the electron exerts on a magnetometer because of the inherent uncertainty in the position and velocity of the electron.

Nevertheless, it seems theoretically possible to detect properties in a beam of electrons due to this spin which would be partly analogous to those of a beam of polarized light. An "unpolarized" beam would be one in which all directions of magnetization were equally probable (with reference to axes moving with the electron), while in a "polarized" beam the magnetic moment would have a preferred direction. Any process which disturbed the uniform distribution of magnetic moments would act as a polarizer and reciprocal process could serve as analyser.

Several such processes have been examined theoretically. Darwin * finds that reflexion from a plane grating could serve if the grating has mixed electrical and magnetic qualities, but not if it has either alone. Frenkel † finds that no such effect occurs on reflexion at a surface of discontinuity, and Förster has extended this to the case of a potential barrier (*Zeit. f. Phys.* lxxxv. p. 514 (1933)). On the other hand, Mott ‡ finds that nuclear scattering ought to produce an appreciable asymmetry of the scattered beam if certain conditions are fulfilled. This asymmetry can be shown by a second scattering under similar conditions which would yield different numbers of electrons according to whether the second scattering is in the same or the opposite direction to the first. The asymmetry is thus one of 180° round the axis of the beam

* Darwin, *Proc. Roy. Soc. cxx.* p. 631 (1928).

† Frenkel, *Compt. Rend. clxxxviii.* p. 153 (1929).

‡ Mott, *Proc. Roy. Soc. cxxxv.* p. 429 (1932).

and not 90° as in the case of light or X-rays. Mott's conditions are:—

- (1) The scattering must be through large angles comparable with 90° .
- (2) The scattering nucleus must be of large atomic number.
- (3) The speed of the electrons must be comparable with that of light.

In the particular case of two right-angled scatterings by gold nuclei, Mott finds that the ratio of electrons scattered twice the same way to those scattered first one way and then back again is $(1 + \frac{1}{2}d)/(1 - \frac{1}{2}d)$ where d is given in the table.

Energy in kilovolts.....	10.5	25	45	79	127	204
Per cent. polarization ...	0.5	0.2	3.0	11.5	15.5	14

The maximum d , 15.5 per cent. occurs at 137 kv., but the variation is slow and at 100 kv. d is 14.2 per cent.

A number of experiments have been made to test these and other theories. Davisson and Germer * have examined the double reflexion of slow electrons from single crystals of nickel arranged as in the familiar Norrenberg experiment. No 90° effect was found, and the 3 per cent. 180° effect observed was probably experimental. Here selectively reflected electrons were used; Rupp †, using irregular reflexion, also found no effect on copper up to 380 volts. The first experiments with fast electrons were made with β -rays by Cox, McIlwraith, and Kurrelmeyer ‡, and continued by Chase §. The effect found, about 4 per cent. in the opposite direction to that predicted by Mott, was considered to be instrumental. In these experiments the targets were thick, so that most of the scattering must have been multiple, and Mott's first condition was only apparently fulfilled. Using very small angles of reflexion $\sim 1^\circ$, Rupp || found an apparent dissymmetry with cathode rays. To test this the author ¶

* Davisson and Germer, *Phys. Rev.* xxxiii. p. 760 (1929).

† Rupp, *Zeit. f. Phys.* liii. p. 548 (1929).

‡ Cox, McIlwraith and Kurrelmeyer, *Proc. Nat. Acad. Sci.* xiv. p. 544 (1928).

§ Chase, *Phys. Rev.* xxxiv. p. 1069 (1929).

|| Rupp, *Zeit. f. Phys.* lxi. p. 158 (1930).

¶ Thomson, 'Nature,' cxxvi. p. 842 (1930).

examined the rings formed when a beam of cathode rays scattered or diffracted by one gold film is diffracted by a second. These rings were, however, uniform as far as could be detected photographically for electron energies up to 70 kv. Kirchner* found a similar result, and Rupp † has since suggested a possible instrumental explanation of the effect he found.

More recently two groups of papers have appeared. In the one Langstroth ‡, Dymond § and Rupp || have examined the double right-angled scattering of cathode rays by metals in attempts to test Mott's theory. Langstroth, working with thick tungsten targets and 10 kv. electrons, found, as might be expected, no effect. Dymond used thin gold so that the scattering was single. His method was to compare the asymmetry of 70 kv. electrons with that for 20 kv., which he assumed to be small as predicted by Mott. Dymond found an excess asymmetry of 1.7 per cent. in the right direction, but there were large asymmetries up to 10 per cent., even with the slow electrons, and the results could also be explained by saying that the effect of instrumental asymmetry increased slightly with the energy of the electrons and that there was no true polarization, or again, that it decreased with energy and that the polarization was considerably larger than the figure given. Mott's theory gives 10 per cent. for 70 kv. Rupp || works with electrons of 20–250 kv. scattered first by a fairly thin foil of gold (about $1\ \mu$) and then by a gold wire. His method also is comparative, it being assumed that when the gold wire is replaced by aluminium the asymmetry found is wholly due to instrumental causes which can accordingly be eliminated. In making the adjustments it is also assumed that for 20 kv. there is no polarization even with gold. Rupp finds 3.8 per cent. polarization for 130 kv. and 9.6 per cent. for 250 kv. There is thus no sign of Mott's maximum at 137 kv., and even at 250 kv. the polarization is too low. Two criticisms suggest themselves to these experiments. In the first place the analyser was massive and the scattering must have been mostly plural,

* Kirchner, *Phys. Zeit.* xxxi. p. 772 (1930).

† *Zeits. f. Phys.* lxxix. p. 652, note (1932).

‡ Langstroth, *Proc. Roy. Soc.* cxxxvi. p. 558 (1932).

§ Dymond, *Proc. Roy. Soc.* cxxxvi. p. 638 (1932).

|| Rupp, *Zeits. f. Phys.* lxxix. p. 642 (1932).

which on Mott's view would give little asymmetry. Secondly, if Mott's theory is wrong in some respects it may be wrong in others, and the assumption that aluminium gives much less polarization than gold becomes doubtful.

The other group of experiments are by Rupp and Szilard *. A beam of cathode rays was reflected through 90° by a massive gold target and then diffracted by a thin gold foil. The outer rings (*e. g.*, $\sqrt{19}$, $\sqrt{20}$, and $\sqrt{24}$) showed an asymmetry when the voltage exceeded about 100 kv., being blacker on the side corresponding to two deflexions in the same direction. This asymmetry rotated with the Larmor precession when a longitudinal magnetic field was applied between the two scatterers, was extinguished by a transverse magnetic field of suitable strength in the plane of scattering, and reversed by one of twice the strength.

The object of the present work was double: to investigate this latter effect, using a thin film for the first scatterer †, and to test Mott's theory for the voltages for which it predicts a large dissymmetry, without, if possible, making any assumptions as to the behaviour at other voltages.

Apparatus.

(1) *Generator*.—The high-tension current was produced by a transformer giving 80 kv. rectified by a valve and smoothed by a condenser. For this apparatus I am indebted to a grant from the Royal Society. The voltage was doubled by using a second valve and condenser in the manner described by Cockcroft ‡. The voltage was measured by a spark gap (5" copper spheres) and the current by a milliammeter on the earthed side of the condenser. A constant voltage was maintained by a rheostat and voltmeter in the field current of the low potential generator.

(2) *Discharge-Tube*.—A porcelain cylinder A (fig. 1), 55 cm. long and 10 cm. internal diameter, was closed at the top by a mild steel plate through which passed a

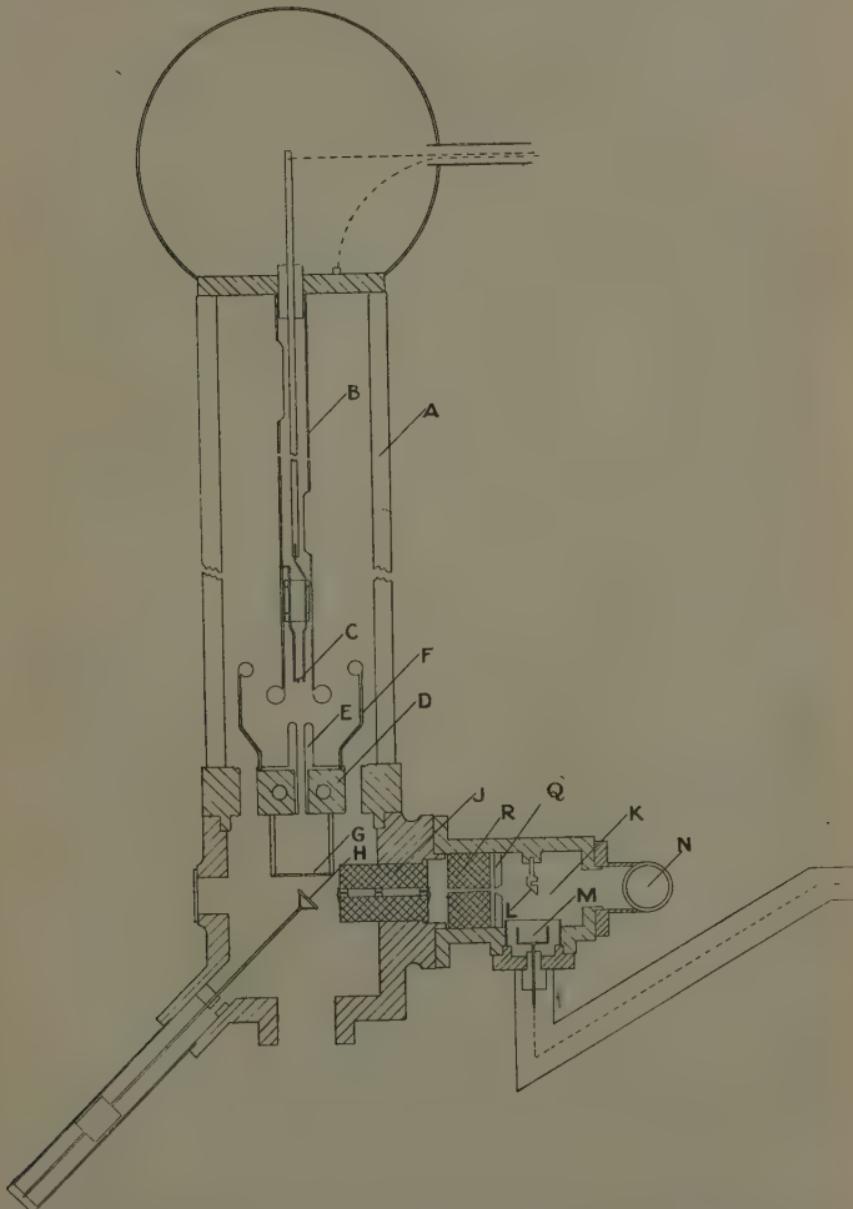
* Rupp, *Naturwiss.* xix. p. 109 (1931); Rupp and Szilard, *ibid.* p. 422; Rupp and Szilard, *Phys. Zeit.* xxxiii. p. 158 (1932); Rupp, *ibid.* p. 937.

† A preliminary account of this has appeared in 'Nature,' 1933.

‡ Cockcroft, *Proc. Roy. Soc. cxxix.* p. 477 (1930).

steel tube B carrying at its lower end a tungsten filament C of S form, the other end of which was attached to a wire

Fig. 1.



which passed back up the steel tube from which it was insulated by steatite. Insulated accumulators lit the filament. The cylinder stood on a water-cooled brass

base D covered with a copper disk in good thermal contact. The disk carried a copper anode E, pierced with a 5 mm. hole. A copper cylinder F surrounded the anode to prevent stray electrons getting through the holes in D through which the tube was exhausted. Anode, cylinder, and the end of the steel tube with its stress distributor were degassed in a vacuum furnace and with an induction heater.

(3) *Polarizing Chamber*.—After passing through the anode the electron struck a molybdenum plate G with a 1.5 mm. hole, which could be closed by a magnetically operated shutter. Those that passed through struck the target film H which was rotated magnetically so as to prevent the rays piercing it, and to average irregularities, by changing the point of impact. Scattered rays then passed into the canal in the lead block J, in front of and behind which diaphragms could be placed. The chamber stood on an oil-diffusion pump of the Burch type. The earth's magnetic field was neutralized with Helmholtz coils.

(4) *Diffraction Camera*.—For the first experiment a diffracting film of gold made by sputtering in the usual way * was mounted close to the second diaphragm. A simple camera of the usual type with plate holder and willemite screen was joined to the polarizing vessel by a flat metal-to-metal ground-joint. The camera was exhausted by a separate oil-diffusion pump. The distance from film to photographic plate was 28.9 mm.

(5) *Analysing Chamber*.—For the later experiments the diffraction camera was replaced by the analysing chamber K containing the analysing gold film L, and the Faraday cylinder M. For these experiments the beam was limited by lead plugs in J, pierced with holes 0.3 mm. in diameter. The lead block P and aluminium disk Q served to stop scattered radiation. A beaten gold film 5.3×10^{-6} cm. thick was mounted in front of M to stop slow secondary electrons. The whole chamber could be rotated between the two ground plates which attached it respectively to the polarizing chamber and to an oil-diffusion pump N.

* Thomson, Proc. Roy. Soc. exxv. p. 352 (1929).

(6) *Electrometer and Leads.*—A rigid wire in an earthed metal case led from the Faraday cylinder to the measuring system. The case was arranged so that part of it would turn with the analysing chamber without disturbing the rest, and a spiral spring in the lead itself took up the twist. The current of the order 10^{-14} amp. was measured by means of an electrometer valve which was shunted with a resistance of 2×10^{12} ohms of the Krüger type. In a valve of this kind the grid when insulated takes up a positive potential; by "earthing" the grid through a potentiometer adjusted to about this positive potential the instrument can be brought more quickly to its zero. The plate current was fed directly to a galvanometer of 6.5×10^{-10} amps. per div. sensitivity and 376 ohms resistance, which was usually shunted with 20–250 ohms.

Experimental Methods and Results.

(1) *Diffraction Experiment.*—It was not easy to get sufficient intensity in the diffracted patterns, and the exposures were rather long, 1 hr.– $1\frac{1}{2}$ hrs. The gold film used for the polarizer had a thickness of 1.23×10^{-4} cm.; this satisfies the Wentzel criterion of single scattering for 150 kv. electrons, but without much to spare. The analysers were sputtered films of the usual type, their thicknesses were not measured, but must have been of the order 2×10^{-6} cm. Two diaphragms, 3 mm. diameter and 6 cm. apart, limited the beam; with such large holes the rings of the diffraction pattern were broad and close rings were not resolved. I found the energy of the rays by measurement of the rings, using the de Broglie law with correction for relativity, and taking the cube side of gold as 4.06×10^{-8} . After each exposure the film was turned through 180° in its own plane, but this precaution was apparently unnecessary.

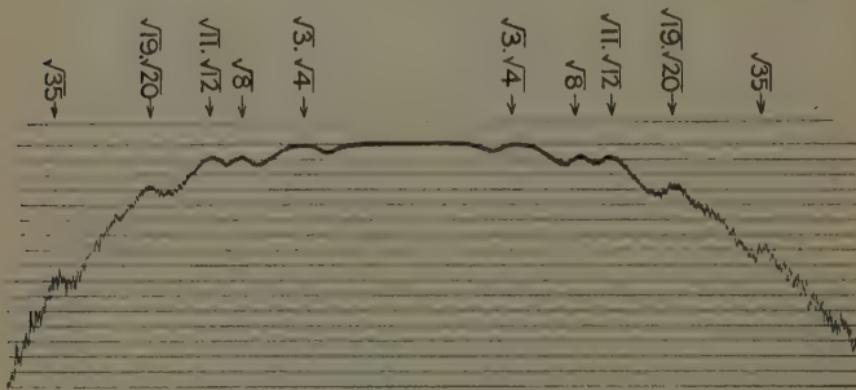
No dissymmetry of the kind found by Rupp could be detected by eye in any of the eight plates which were taken with three diffracting films with voltages from 147 to 161 kv. (mean 152.4).

Density measurements were made on four of the best plates across the diameter in the plane of symmetry, with the object of seeing if there was any appreciable difference on the two sides. Readings were taken at $\frac{1}{2}$ mm. intervals with a Toy and Rawlins photometer.

This is a tedious process, but much more sensitive than using a recording photometer, the readings of which are by no means proportional to the density. No asymmetry could be detected in the rings, even in $\sqrt{24}$, $\sqrt{27}$, and $\sqrt{35}$, $\sqrt{36}$. The background in the earlier plates showed marked asymmetry, even with a recording photometer, an effect due to X-rays. By using plenty of lead to shield the camera this asymmetry was almost entirely avoided.

Finally, two plates (voltages 153 and 154 kv.) were taken with a solid polarizer as used by Rupp. This gave much greater intensity of scattering, and it was possible to use diaphragms of 15 mm. diameter which greatly improved the sharpness of the pattern; but there was

Fig. 2.



Both scatterings in same direction at this end.

Scatterings in opposite directions at this end.

still no sign of dissymmetry in the rings, as is shown from the photometer curve (fig. 2) taken from one of them.

(2) *Experiments with Electrons scattered twice through 90°.*

Since Mott's theory predicts a polarization of 14 per cent. at 100 kv. and only 15.5 per cent. at 137 kv., where the effect is a maximum, it seemed best to work at the lower voltage as it is easier to keep the discharge steady and prevent sudden gas discharges which seriously upset the electrometer valve. In addition, the currents are larger, and can be measured with greater accuracy.

In order to eliminate the ionization due to X-rays, which at 100 kv. produced large spurious currents, all the wires connected to the grid of the electrometer, the

electrometer itself, and the high resistance were shielded with 1 cm. of lead, and thick blocks of lead were arranged round the base of the porcelain tube. When this was done, the current with the second scattering film removed was small (of the order of 3 per cent. of the current with the film in place) and sensibly the same for the two positions of the analysing chamber. No correction was therefore required on account of X-rays or electrons scattered by the film holder.

The chief sources of error are the shift in the zero of the electrometer and the change in the current given by the discharge. The time constant of the system consisting of the Faraday cylinder, leads, electrometer, and high resistance was about 100 secs., and a compromise had to be made between speed in taking the readings and allowing time for the system to reach its steady state. The following method of taking the readings was found the most satisfactory. After taking the zero with the system insulated and the discharge off, the potentiometer was adjusted so that the "earthing" zero was within a few divisions of the true zero. The discharge was then switched on, and when it was steady the system was insulated by breaking the connexion between it and the potentiometer. After two minutes by stop-watch, by which time the spot on the galvanometer scale was moving quite slowly, the reading was taken.

The spot was then brought back quickly to near its zero by the earth connexion, the discharge stopped and the true zero taken. As the difference was usually quite small, $1\frac{1}{2}$ min. wait in the insulated condition was enough to find the zero with sufficient accuracy. The potentiometer was then reset, if necessary, and the process repeated. After the two readings, with their zeros, the analysing chamber was turned into the reverse position. A short wait was necessary to allow slight piezoelectric effects to disappear, and another pair of readings was then taken, when the analysing chamber was again reversed. Two pairs of readings in the "Up" and one in the "Down" positions, or two "Down" and one "Up," constituted a "set." In some of the earlier sets three readings were taken in each position, the insulated zero being taken at the beginning and again at the end of the three. In the course of a set of readings the current in the discharge often changed by about 5 per cent. This change was

carefully watched and was always sensibly uniform, so that its effect would be eliminated by meaning. The high tension currents used ranged from about 2 to about 5 millamps.

Results at 30 kv.

The first task was to show that there is no polarization at low voltages, *e. g.*, 30 kv. For this the films need to be thin to ensure single scattering. Measurements were made with a pair of 1.3×10^{-5} cm. (thickness found from optical density).

These gave the following results for varying currents in the Helmholtz coils :—

Current in coil.	mm. galvanometer deflexion.		Ratio.
	Faraday cylinder up.	Faraday cylinder down.	
none	259	280	.925
.3 amp.	318	318	1.00
.7 amp.	261.5	266	.993
1.0 amp.	348	350	.985 mean .994

There is thus no appreciable dissymmetry when the current exceeds .3 amp. A current of .7 amp. gave the best compensation on a dip needle placed near the analysing chamber, and was used throughout afterwards. The following results were found with thicker foils :—

Thickness.	mm. galvanometer deflexion.		Ratio.
	Cylinder up.	Cylinder down.	
2.4×10^{-5}	$\left\{ \begin{array}{l} 364 \\ 380.7 \end{array} \right\} 372.3$	376.7	.988
2.4×10^{-5}	$\left\{ \begin{array}{l} 502 \\ 433.7 \end{array} \right\} 467.7$	442	1.056
$.9 \times 10^{-5}$	$\left\{ \begin{array}{l} 478.5 \\ 457.0 \end{array} \right\} 467.7$	$\left\{ \begin{array}{l} 451.7 \\ 477.0 \end{array} \right\} 464.3$	1.007
		Mean ..	1.017

The scattering would be mostly single, even with the thickest of the above foils, but the results are chiefly important as showing that there was no appreciable dissymmetry in the apparatus when the thicker foils were fitted. All these foils were prepared by sputtering in

the usual way. They were free from visible holes. The thicknesses of the last two were found by weighing; they were used for the experiments at 100 kv., at which voltage they easily fulfil Wentzel's criterion for single scattering. In every case the polarizing and analysing films were of equal thickness and made from the same piece.

Results at 100 kv.

The following table shows the results near 100 kv. The voltage was measured by sparkgap after the runs and varied from 102 to 105 kv. Two sets of readings with the 1.3×10^{-5} cm. film gave ratios .92 and 1.03 respectively. These are less accurate than those in the table as the currents were less, and a considerable correction was required for the effects of X-rays which had not been entirely eliminated when they were made:—

Thickness of film.	mm. of galvanometer deflexion.		Ratio.
	Cylinder up.	Cylinder down.	
2.4×10^{-5} cm.	$\left. \begin{array}{l} 325 \\ 272 \end{array} \right\} 298.5$	313.3	.955
	$\left. \begin{array}{l} 243.3 \\ 234 \end{array} \right\} 238.6$	231	1.033
	$\left. \begin{array}{l} 203.5 \\ 186.5 \end{array} \right\} 195$	195.8	.996
	176	$\left. \begin{array}{l} 177.2 \\ 167.8 \end{array} \right\} 172.5$	1.020
	156.5	$\left. \begin{array}{l} 169.2 \\ 147.8 \end{array} \right\} 158.5$.987
		Mean998
1.9×10^{-5} cm.	149.5	$\left. \begin{array}{l} 162 \\ 143.5 \end{array} \right\} 152.7$.979
	173.7	$\left. \begin{array}{l} 164 \\ 165.5 \end{array} \right\} 164.8$	1.053
	$\left. \begin{array}{l} 160.5 \\ 169.7 \end{array} \right\} 165.1$	175	.942
	157.7	$\left. \begin{array}{l} 153 \\ 159.2 \end{array} \right\} 156.1$	1.010
	158.0	$\left. \begin{array}{l} 160.5 \\ 160.5 \end{array} \right\} 160.5$.985
		Mean ..	.994

Mean of both films .998 : .01. Thus there is no appreciable polarization. Mott's result would require a ratio of 1.14.

Discussion.

The absence of any effect of the kind found by Rupp is not unexpected on theoretical grounds, as one would not expect scattering through an angle of the order of 1° to show much asymmetry even in a strongly polarized beam. It should, however, be mentioned that the voltage at my disposal was smaller than that used by Rupp, which was usually 220 kv., and that he found the effect only beginning at 150 kv. Against this must be set the fact that I was able to use a thin target for the initial scattering, and to observe the larger rings, both of which should have increased the effect. The most probable explanation of Rupp's observations is that they were caused by a non-uniform background of scattered electrons. Since the response of a photographic plate is not a linear function of the intensity of the rays, differences in the background can produce differences in the apparent blackness of a ring which is really uniform. This does not, however, explain Rupp's observation with the transverse magnetic field except in so far as this necessarily involves some alteration in the paths of the electrons.

We have seen that there is no polarization of the kind required by Mott's theory within the limits of the probable error, which we may take as ± 1 per cent. Certainly the 14 per cent. effect required by the theory does not exist. Most of Mott's work has been, I understand, checked independently; but unless there is some error in the calculations, we are driven to the conclusion that Dirac's theory cannot be applied to the problem of scattering by heavy atoms. It seems very unlikely that the presence of the outer electrons can make much difference to the scattering, which must be almost entirely nuclear. The nearest distance of approach for 90° scattering at 100 kv. is 2.3×10^{-11} cm., which is well inside the K ring. All the conditions of Mott's calculation were fulfilled in these experiments, but it seems possible that Dirac's theory does not hold in the intense field close to a gold nucleus where, of course, most of the scattering takes place. It is probable that an electron with sufficient energy can cause a breakdown in the medium in such a region and produce a pair of positive and negative electrons, as

quanta are known to do. While the electrons I used would certainly not be able to do this, it is not unreasonable to suppose that the Dirac equation ceases to hold exactly for energies much below those required to cause a breakdown. It is, however, surprising that the effect should be just to cancel the polarization, and one is inclined to surmise that the polarization of a free electron may be among the unobservables.

Note added in proof.—I have been able to take a few sets of readings at about 120 kv. Here there is a considerable X-ray correction even with the thick lead used. The thickness of the films was 3.4×10^{-5} cm.

Cylinder up.	Cylinder down.	Ratio.
397.2×63.7 (due to X-rays)... = 480.9	381.7×71.1 (due to X-rays)... = 452.8	1.017
$358.2 \times 63.7 = 421.9$	$338.3 \times 71.1 = 409.4$	1.030
$368.2 \times 63.7 = 431.9$	$353.0 \times 71.1 = 424.1$	1.017

The probable error must be about 2 per cent. due to the correction, but the results show that the divergence from Mott's result persists at higher voltages.

Summary.

Two types of polarization experiment are described. In the first electrons are scattered at right angles, and then diffracted by a thin film. In the second they are scattered twice at right angles in the same plane. In neither case was any asymmetry observed. In the first case the voltage was 153 kv., in the second 30 kv. and 103 kv. The second result is contrary to Dirac's theory of the electron.

I wish to express my sincere thanks to Mr. C. R. Burch for advice on the working of the pumps, and to Mr. H. Hutchinson for his assistance with the apparatus.

XC. *The Molecular Refractivity of Sodium Chloride.* By
 F. H. NEWMAN, *D.Sc., F.Inst.P., Professor of Physics,
 University College, Exeter* *.

THE additive principle, which is applicable to many properties of solutions, depends upon the hypothesis of the practical independence of the constituents within the solution. Applied to optical properties, a relationship between the optical and chemical behaviour of a substance must be formulated which is independent of temperature, state of aggregation, and other physical properties. Such a relationship is the Lorentz expression for specific refraction, viz., $(\mu^2 - 1) / (\mu^2 + 2)\rho$, which is a very characteristic quantity for a given substance and is even independent of the wave-length of the light selected for measuring the refractive index, provided that the wave-length is long.

It is well recognized that the refractive index of an electrolytic solution does not vary at the same rate as the percentage composition or the concentration. This is due, in part at least, to the fact that when a salt is dissolved the contraction, or expansion, during solution per unit quantity of salt varies with the concentration of the solution, but with dilute electrolytic solutions, where the degree of dissociation is large, the increments of refractive index with changing concentration, if referred to molecular quantities of salt, show distinctive additive properties. This is to be expected if the property is ionic rather than molecular. The additive relationship should be most satisfactory at infinite dilution, but the difficulty of obtaining sufficiently accurate measurements makes the verification as a rule less satisfactory with very dilute solutions.

The Lorentz expression is based on certain assumptions, and was derived strictly for a system consisting only of particles of the same kind, so that in any complicated system molecular refraction would not be expected to show strict additivity. Applied to ions in solution there must be some mutual action between any ion and the surrounding medium. There is, for example, the polarization of the ions in the electric field of the light-waves

* Communicated by the Author.

and the deforming action of the electric field of the ions in the absence of light.

The refractivities of ions, of which the structure is analogous to that of the inert gases, have been calculated both from experimental results and theoretical considerations. For example, Heydweiller *, Fajans and Joos †, and Wasastjerna ‡ employ the additive law to salt solutions, or small crystals, but it is necessary to assume some one ion as having a known refraction so that, subtracting this value from that of the salt, one obtains the refraction of the other ion. Thus the experimental values for ionic refractions depend upon the value assumed for the known ion and, in addition, there is always a more or less uncertain correction for the effect of hydration. It is certain that the electrostatic interaction of the ions on one another, as well as on the surrounding dipole molecules of water, is accompanied by polarization phenomena. The cations exert attractive forces on the electron shells of the anions, or of the water-molecules surrounding them, and deform them to some extent. In this way the ionic refraction is changed. The dielectric constant of a liquid when a readily ionized salt is dissolved therein is lowered. Such a lowering has been attributed by Sack § to the saturation of the molecule of the liquid by the intense fields arising from the dissolved ions.

Fajans, Kohner, and Geffcken || measured the molecular refraction of sodium chloride over a concentration range from two equivalents per 1000 gm. of water up to saturation. The molecular refractions thus obtained at various concentrations, when plotted as a function of the concentration, showed a regular negative rate of change from which extrapolation to infinite dilution was carried out. They obtained the value 9.27 for the sodium yellow radiation at 25° C. They also found that

$$\Delta R = -0.053,$$

where

$$\Delta R = R_{5N} - R_0,$$

R_{5N} being the molecular refraction at 5N concentration and R_0 that at infinite dilution. So that with increasing concentration there is a definite decrease in refraction,

* *Phys. Zeits.* xxvi. p. 526 (1925).

† *Zeits. f. Phys.* xxiii. p. 1 (1924).

‡ *Phys. Ber.* v. p. 226 (1924).

§ *Phys. Zeits.* xxviii. p. 199 (1927).

|| *Zeits. El. Chem.* xxxiv. p. 1 (1928).

i. e., a net consolidation in the case of the easily deformable anion Cl^- with the less deformable Na^+ cation.

In the crystalline state the ions may be considerably distorted by inter-atomic forces, and one fact which shows that the perturbing effects in crystals are large is the considerable deviation from additivity exhibited by their molecular refraction, amounting to as much as 1.5 units for the alkali halides *. According to Born and Heisenberg †, the values for the ionic refractions of Na^+ from various salts are 0.48 (NaF), 0.53 (NaCl), 0.51 (NaBr), 0.33 (NaI) respectively, the contribution made by the F^- , Cl^- , Br^- , and I^- ions being taken into account.

Pauling ‡ and Van Vleck § from quantum mechanics have derived theoretical values for the screening constants of atoms and ions to be used in the equations representing molecular refraction—the assumption being made that the nuclear charge is large in comparison with the charge of an electron shell. Actually this requirement is not well fulfilled by actual atoms and ions, but from a comparison with the accurately known experimental values of the molecular refractions of the rare gases and of some ions in aqueous solution, it is found that the calculated values of the molecular refraction screening constants are practically correct. By employing the indicated corrections theoretical values are obtained for the refraction of ions. The formula deduced is

$$R = 0.0470 \times n^4 (15n^2 + 21) \sum_{\kappa} \frac{1}{(Z - S_{\kappa})^4},$$

where the summation is to be taken over all electrons in the n th shell. R is the ionic refraction, S the ionic refraction screening constant, Z the atomic number, and n the principal quantum number. Thus for neon $n=2$, $l=0, 1$ (the old azimuthal quantum numbers), $S_{nl}=4.45, 5.64$, the two values representing the sub-shells having the same value of n . For argon $n=3$, $l=0, 1$, $S_{nl}=9.70, 10.99$. Introducing these values into the above equation, the predicted ionic refractions are Na^+ 0.457, Cl^- 8.92, whereas from Heydweiller's tables, assuming 2.17 for the potassium ion, the experimental values in solutions are

* Spangenberg, *Zeits. f. Krist.* liii, p. 499 (1923).

† *Zeits. f. Phys.* xxiii, p. 388 (1924).

‡ *Proc. Roy. Soc. oxiv*, p. 181 (1927).

§ *Proc. Nat. Acad.* xii, p. 662 (1926).

Na^+ 0.11, Cl^- 8.76, giving the molecular refraction of NaCl at complete dissociation equal to 8.87. These predicted values for the ions apply only to free ions in the gaseous state, and in general, comparing these values with the experimental results obtained for the alkali halides in solution and in the crystal form, it appears that ions in solution are more similar to gaseous ions than ions in crystals, so far as molecular refraction is concerned.

Recently the refractive index of aqueous solutions of sodium chloride has been measured in these laboratories by Mr. H. Walke at concentrations within the range 0.002–0.0001 equivalent per 1000 grams of water. A Rayleigh refractometer was used and the measurements were made at 18° C. with the D-lines of sodium. The results, which will be published in a subsequent paper, show that there is a change in the molecular refraction of the solution at concentrations below 0.0005 equivalent per 1000 grams of water. Dissociation appears to be complete below this concentration. The specific refraction of the sodium chloride in this completely dissociated condition has been calculated from the formula

$$k_1x + k_2(100-x) = k_3 100,$$

where k_1 , k_2 , and k_3 represent the specific refractions of the solute, solvent, and solution respectively, and x is the percentage of salt by weight. The molecular refraction of NaCl at infinite dilution has been found in this manner to be 9.05 at 18° C. for the D-lines, whereas the value predicted by Pauling is 9.38 and that from Heydweiller's tables 8.87. Walke's measurements indicate that the value cannot be accurately obtained by extrapolating values at more concentrated solutions. A definite change in the molecular refraction appears at concentrations below 0.002 equivalent per 1000 grams of water. It is to be expected that for more concentrated solutions, when the ions approach more closely to each other and thereby displace the water, uniting to form undissociated molecules, there should be perceptible changes of the refractivity. In addition, it must be remembered that the hydration of the Na^+ ion is considerable; Remy*, for example, has estimated that there are on an average 7.4 water-molecules attached to each Na^+ ion.

* Trans. Farad. Soc. xxiii. p. 387 (1927).

XCI. *Notices respecting New Books.*

Tables for the Development of the Disturbing Function. By E. W. BROWN and D. BROUWER. [Pp. 157.] (Cambridge University Press, 1933. Price 10s. 6d. net.)

Of even greater importance than the actual computation of tables is the "staff work" that must precede the compilation. Errors, provided that they are not systematic or so numerous as to make the tables worthless, can usually be detected by differencing, supplemented possibly by the recalculation of a few pivotal values: but a table badly designed, arranged, or printed can be a source of perpetual annoyance. The tables under consideration have both the originality and the experience of Dr. E. W. Brown in their inception. They aim at giving the coefficients in the development of the disturbing function without recourse to anything more than linear interpolation, and with this end in view those factors of the coefficients which vary rapidly with the argument are separated from the more slowly varying ones; since the rapidly varying part is easily calculable, it is sufficient to construct tables for the part that varies slowly.

The logarithms of these functions are printed, together with the first differences. The paper is good and the typography and arrangement excellent; mistakes are unlikely to be caused by similarity of figures. It is of special interest that the sub-tabulation to tenths was done by the use of the Hollerith machines of the Statistical Bureau of Columbia University, New York City; after various methods of interpolation had been tried, Dr. Comrie's method of end-figure interpolation (as adapted by Comrie for the Hollerith machine) was adopted.

There are special tables for the calculation of the perturbations of Jupiter and Saturn, and likewise tables of the values of the equation of the centre and of the radius vector, in powers of the eccentricity, for special values of the mean anomaly. Schedules are given for numerical harmonic analysis, and also an account of the procedure for double harmonic analysis.

Matière et Energie. Par VICTOR HENRIE, Professeur à l'Université de Liège. [Pp. 436+91 figs.] (Paris: Hermann et Cie. Price 110 francs.)

THIS book of ten chapters is an exposition of modern Atomic Physics on usual and well accepted lines.

Starting with the atomic theory and the periodic classification of the elements, Professor Henrie follows up the results

of the Moseley discovery, discusses in detail radioactive elements and isotopes, and concludes with chapters on kinetic theory and atomic structure.

A most useful book for students, yet it suffered from a minor—yet very important and tiresome—defect, the pages were uncut!

The book is a most useful one for students of Physics—especially in regard to the bearing of Atomic Physics on Chemistry.

Infra-red Photography. By S. O. RAWLING, D.Sc. [Pp. 56+ 28 figs.] (Blackie & Son, 1933. Price 3s. 6d.)

THIS little book is a popular description of the present state of infra-red photography.

The early pioneer work of Professor R. W. Wood is handsomely acknowledged in the preface, where it is pointed out that this brilliant experimental physicist, a quarter of a century ago, was taking infra-red photographs.

The only new point is the actual production of suitable plates and infra-red sensitive materials on a commercial scale.

The author has kept before him all the time the view-point of the general reader with the result that, while practical details and information abound, only a very general account of underlying principles is given. This, of course, in no way detracts from the value of the book to the general reader who may wish to make an attempt at practising the art himself.

After a few introductory pages, a chapter is devoted to the materials available for sensitizing plates in the infra-red, followed by a chapter on dark room illumination, types of camera, and development.

The last chapter is on the applications of infra-red photography and takes up about two-thirds of the volume.

Haze penetration, photography of old manuscripts, micro-photography, are just a few of the matters discussed.

There are some useful appendixes on points of practical interest.

The book is well illustrated, pleasantly written, and nicely produced.

Das Kausalgesetz und seine Grenzen. By PHILIPP FRANK. [Pp. xv+308.] (Vienna : Springer, 1932.)

In this book, the sixth volume of the series *Schriften zur wissenschaftlichen Weltauffassung*, edited by Frank and Schlick, Frank has given a detailed discussion of the significance of causality for science. His return to a problem which engaged his attention some twenty-five years ago has been stimulated partly by the development of quantum mechanics,

and partly by the retrogressive character of some of the quasi-philosophic speculation to which this has led.

The attitude adopted, in keeping with that of the Vienna circle, is that the study of the significance of concepts which are used in science should be carried out by the ordinary methods of scientific reasoning; it is as illegitimate as it is unnecessary to hand over the problems of interpretation which arise to be considered on a "higher plane" of philosophy.

Frank divides significant statements into tautologies (such as the propositions of logic and mathematics) and statements of fact (*Wirklichkeitssätze*) about the actual world. There is a tendency for general laws to become tautological (as does the law of conservation of energy, if energy is virtually defined as being conserved) when they cease to be statements of fact about the world of experience. Frank shows that the law of causality in its very general form, that everything is determined, is either a pure tautology (saying no more than that there is the one particular sequence of events which actually happens) or a statement of fact which implies the existence of a superhuman intelligence. The general law is neither postulated nor implied by science. If the law of causality is regarded as a statement as to how far men can predict future from present experiences, the limitations of the law at once becomes apparent.

Detailed consideration is given to the Laplace formulation of the causality law—that, given the present positions and velocities of all the particles in the world, and the laws of force between them, the future, for an all-embracing intelligence, is completely determined. In practice, however, only approximate predictions can be made of average magnitudes (as in statistical treatments and field theories), and then only under limited conditions.

A number of sections are devoted to biological considerations which have seemed to undermine causality. Vitalism and entelechies are subjected to a devastating criticism. Though beliefs may be held as to the existence of a design in the world (which are shown to be meaningless unless an author of the design is also assumed) they cannot be regarded as scientific conclusions.

In quantum mechanics the relation between the symbols and what is experienced is different from that in the classical theory; and an indeterminacy is explicitly recognized. But the causal relations between experiences are essentially of the same kind, and subject to the same limitations. Quantum mechanics gives no ground for the introduction of super-scientific ingressions. Always, Frank points out, during periods of change in physical ideas, when formulations are lacking in clarity, the opportunity is seized for the introduction of mystical elements. "Im Trüben ist gut fischen."

On the one hand, then, Frank stresses the limitations of the causal law in science; on the other, he shows the unfruitfulness of such concepts as final cause, world plan, or atomic soul. It is not possible to summarize Frank's conclusions in a short pregnant statement; he himself is rightly suspicious of such statements purporting to give answers to very complicated questions.

The book is admittedly not written in a strictly systematic manner. The individual sections are largely self contained, being, as it were, short essays on a wide variety of topics from "Finalism and the Quantum Theory," to "Poincaré, Kant, and Lenin," but all relevant to the main theme. Many scientists may fight shy of a work on causality; but there are few whose interest will not be aroused by some of the topics discussed, which are set forth in an excellent table of contents. In every section there is evidence of a sincere and alert thinker, with a freshness of viewpoint, and of a writer who can express his ideas clearly and forcibly. The book as a whole will be full of interest both to those who sympathize with, and those who look askance on, attempts to build up far reaching speculative philosophies on the basis of particular scientific results.

Inversive Geometry. By FRANK MORLEY, M.A., Sc.D. (Cambridge), Professor-Emeritus of the Johns Hopkins University, Research Associate of the Carnegie Institution, and F. V. MORLEY, D.Phil. (Oxford). [Pp. 272.] (Bell.)

PROFESSOR Frank Morley and Dr. F. V. Morley have collaborated together to produce a work of great charm which is sure to appeal to a wide circle of readers, not only to mathematicians whose main interest is geometry, but also to others. The perusal of the book does not call for any large body of specialist knowledge previously known. It can be profitably read by any capable well-instructed second year's mathematical student reading for an Honours degree at a University. The subject-matter is a compound of geometry and algebraic results geometrically interpreted. There is a large amount of purely geometrical matter, and theorems of purely geometrical statement figure abundantly. Many of these theorems will be already familiar to readers who have read fairly widely in the domain of pure geometry.

The book is divided into two parts. Part I. consists of eleven chapters, and Part II. of ten chapters. The titles of the various chapters are as follows:—(1) Operations of Elementary Geometry; (2) Algebra; (3) The Euclidean Group; (4) Inversions; (5) Quadratics; (6) The Inversive Group of the Plane; (7) Finite Inversive Groups; (8) Parabolic, Hyperbolic,

and Elliptic Geometries; (9) The Celestial Sphere; (10) Flow; (11) Differential Geometry; (12) The Line and the Circle; (13) Regular Polygons; (14) Motions; (15) The Triangle; (16) Invariants under Homologies; (17) Rational Curves; (18) Conics; (19) The Cardioid and the Deltoid; (20) Cremona Transformations; (21) The n -Line. The general scope of the book will now be apparent.

The treatment begins by considering a card turning about a straight edge from one position on a table to another. If a point P of the card lie above a point a on the table and if the edge of the card be l , then after turning the card about l , P will lie above a point \bar{a} on the table, which is defined as the reflexion of the point a in the line l . Thus at the outset the ideas engendered in the mind of the student by his early training in Euclidean geometry are invoked and widened in conception. Thereafter algebraic entities are introduced. They are represented as the points of a plane, and in this plane lies a line on which are represented the real numbers. The parallelogram law for the addition of vectors is introduced and explained, viz., $c=a+b$. Multiplication is represented thus:—If $y=ax$, a triangle x, o, y , is constructed similar to the triangle $1, o, a$; thus being given a and x, y can be obtained by the easy elementary geometry of similar triangles. Also, it is evident that the triangles a, o, y and $1, o, x$ are similar, and hence we can interchange a and x in the above conception. It follows that $ax=xa$ because the same point y is obtained by the two constructions. Thereafter, it is easy to obtain y geometrically from the assignment of x by means of the linear equation $y=ax+b$ (designated a homology). Following this procedure geometrical interpretations and theorems are obtained from the consideration of such algebraic themes:—(i.) the homographic equation $\alpha xy + \beta x + \gamma y + \delta = 0$; (ii.) the quadratic equation, two quadratic equations and their lineo-linear or harmonic invariant; (iii.) the cubic equation, its Hessian quadratic and Jacobian cubic, &c. Among purely geometrical consequences studied may be mentioned (i.) the triangle and its best-known points, lines, and circles; (ii.) Feuerbach's theorem; (iii.) Miquel's theorem that the foci of the five parabolas touching each set of four lines out of a complete set of five lines are concyclic, &c. Some space is devoted to the flow of a fluid.

Throughout the book the presentation is clear and lucid, and the subject-matter is exceedingly well chosen. The reader has no difficulty in sustaining his interest all through its pages.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

FIG. 1.

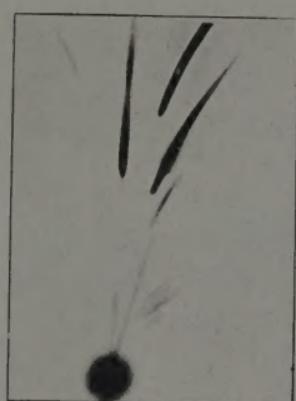


FIG. 2.

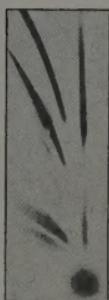


FIG. 3.

